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AN ELECTRON SPIN RESONANCE AND NUCLEAR
MAGNETIC RESONANCE STUDY OF THE REACTION
PRODUCTS OF FORMALDEHYDE AND N-METHYLHYDRAZINE

by

Richard Smith Watkins

United States
Naval Postgraduate School



THEESIS

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MAGNETIC RESONANCE STUDY OF THE REACTION PRODUCTS
OF
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Richard Smith Watkins

December 1970

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An Electron Spin Resonance and Nuclear
Magnetic Resonance Study of the Reaction Products
of
Formaldehyde and N-Methylhydrazine

by

Richard Smith Watkins
Lieutenant Commander, United States Navy
B.S., Bates College, 1961

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the

NAVAL POSTGRADUATE SCHOOL
December 1970



ABSTRACT

An NMR and EPR study of the reaction products of formaldehyde and N-methylhydrazine was conducted primarily to identify the radical species noted when 1,4-dimethyl-dihydro-s-tetrazine was prepared by the oxidation of 1,4-dimethyl-hexahydro-s-tetrazine with mercuric oxide. The radical was deep violet in ether solution, and generated an extremely complex ESR signal. NMR analysis demonstrated that the radical precursor was a reaction side product, and was only present when certain NMR peaks were present. The NMR data coupled with the assignment of the spectrum generated indicated that the precursor was 1,5-dimethyl-hexahydro-s-tetrazine, and the radical was 1,5-dimethyl-verdazyl. This thesis reports the first aliphatic verdazyl. Complete NMR, ESR, and molecular orbital data are documented as is a unique computer method for assigning ESR spectra. In addition, mass spectrographic, UV/visible, IR, and chromatographic methods/data are discussed.

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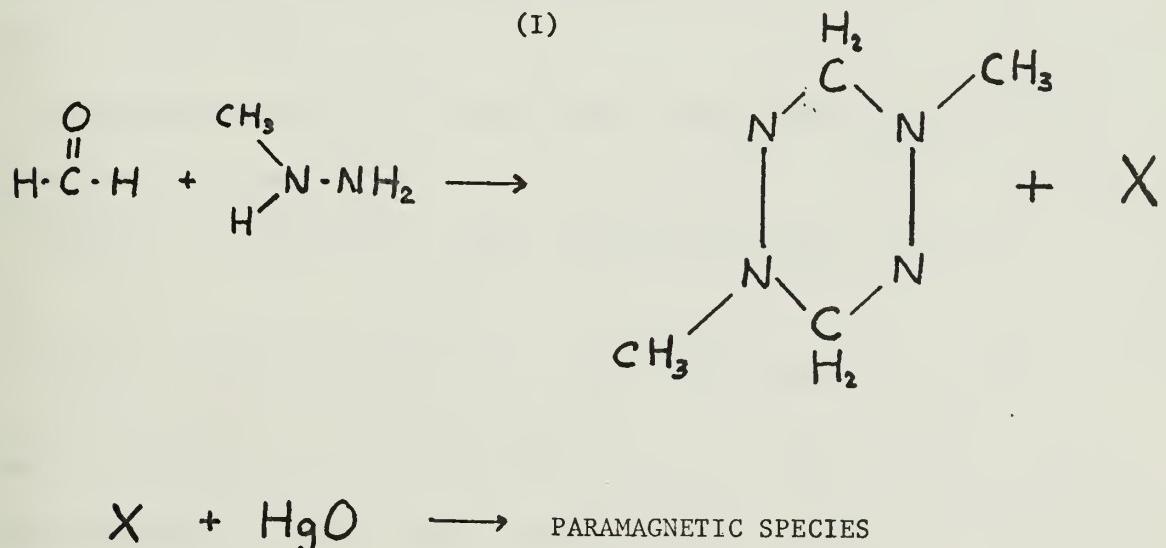
I. INTRODUCTION

A. STATEMENT OF THE PROBLEM

In the preparation of 1,4-dimethyl-1,4-dihydro-s-tetrazine by the oxidation of 1,4-dimethyl-hexahydro-s-tetrazine with yellow mercuric oxide, Tolles¹ et al noted that the ether solution initially turns deep violet with the evolution of some gas when the mercuric oxide is added. This violet ether solution exhibited a very complex electron spin resonance (ESR) spectrum.

This study was designed to identify the radical species and by so doing offer insight into the chemistry of aliphatic methylhydrazones, particularly formaldehyde methylhydrazone.

It has been established that the paramagnetic species is the result of a side product in the reaction between formaldehyde and N-methylhydrazine. This side product frequently remains in evidence after many purification attempts.

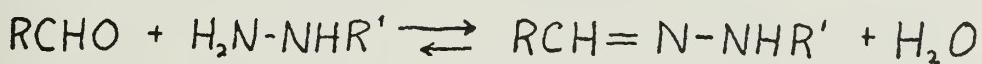


The system defied common physical and chemical separation techniques. Spectroscopic devices were heavily relied upon, in particular electron spin resonance and nuclear magnetic resonance (NMR).

B. HISTORICAL DEVELOPMENT

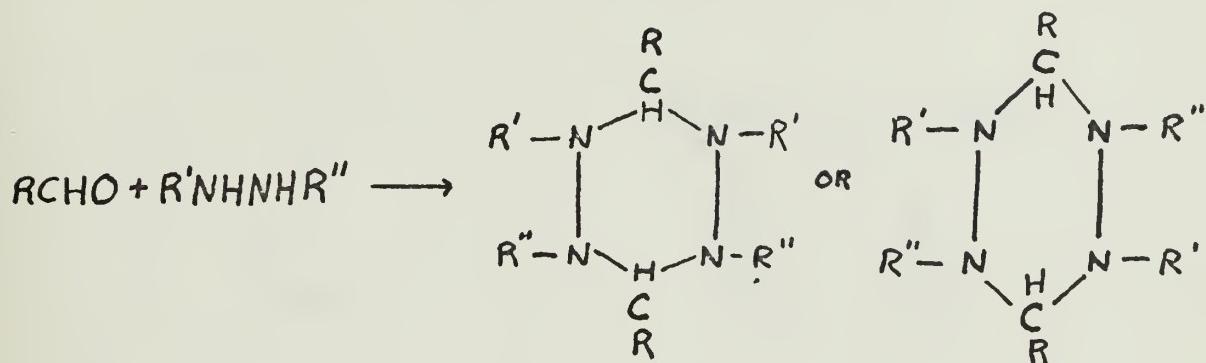
Literature on aliphatic hydrazones was almost non-existent until the early 1950's. Pulvermacher² obtained a condensation product of formaldehyde hydrate in 1893; this product was designated formalazine. In 1912 Hofman and Storm^{3,4} prepared a second formaldehyde derivative of hydrazine, tetraformaltriazine. Klages⁵ et al synthesized the dimethylhydrazones of formaldehyde and acetaldehyde in 1949. Shortly thereafter, Wiley⁶ and associates published an extensive study of aliphatic hydrazones and now a good deal of material is available. This is in sharp contrast to the voluminous material available on aromatic hydrazone chemistry; the first aromatic hydrazone, benzaldehyde methylhydrazone, was reported in 1898⁷. Havens⁸ suggests that the early lack of reliable methods for producing the hydrazines, and the instability of the alkylhydrazones themselves were major contributing factors towards the lack of work in the area of aliphatic hydrazones.

Hydrazones are formed basically from N-substituted hydrazine and aldehydes or ketones.¹⁰



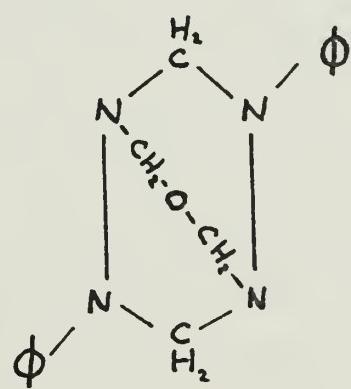
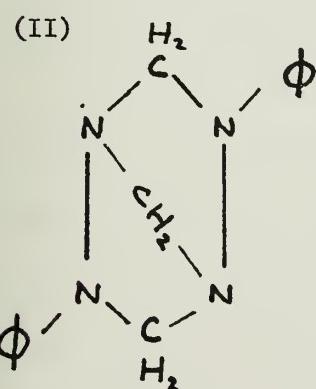
The condensations are reversible but in the case of the aldehyde the forward reaction is more highly favorable than in the case of ketones.⁸

Hexahydro-s-tetrazines are prepared by the reaction of aldehydes, usually formaldehyde, with hydrazines.⁹

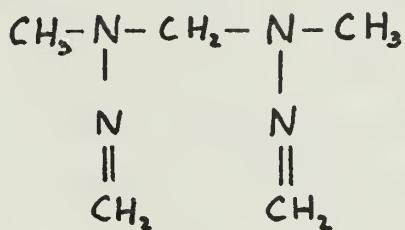
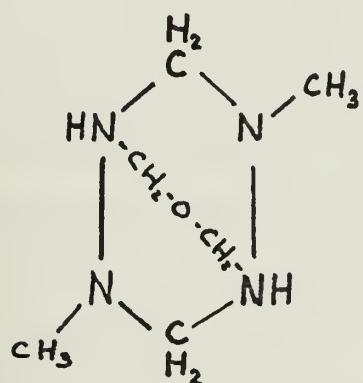


In 1963, Kaufman¹¹ reported the dimerization of N-substituted hydrazones of aldehydes. 1,4-Dimethyl-hexahydro-s-tetrazine (I) is the dimer of formaldehyde methylhydrazone. In his work with heptanal methylhydrazone Havens⁸ noted that the dimer monomerized in an open container at room temperature. The rate of monomerization appeared to be dependent upon sample purity, solvent polarity, and temperature.

Ioffe and Stopskii¹² established that in the preparation of formaldehyde phenylhydrazone the dimer, or 1,4-diphenyl-hexahydro-s-tetrazine (I), was the major product while minor products were evidently products of condensation with excess formaldehyde. Schmitz and Ohme¹³ reported these same condensation products and proposed the following structures:



They extended this study to the reaction products of methylhydrazine and excess aldehyde and proposed the following structures:



They did not suggest a species with a methylene bridge across the unsubstituted nitrogens, although they did in the case of the aromatic substituted species (II).

A fair amount of literature now exists on the chemistry of aliphatic hydrazones. The works of Haven⁸ and King¹⁴ are most extensive, the subject matter includes but is not limited to: preparation of, dimerization and monomerization of, thermal decomposition of, thin layer and gas chromatography of, IR and UV spectroscopy of, and reactions of certain aliphatic hydrazones. They concentrated on the study of heptanalmethylhydrazone. Texts are on the whole rather limited but Smith's Open Chain Nitrogen Compounds Series²⁰ are very informative with regard to reactions including rearrangement, oxidation, and reduction of hydrazones.

Literature investigation indicates that others who did extensive studies on the reactions between aliphatic aldehydes and hydrazines did not report on the reaction of concern. Skorianetz and Kovats^{15,16} showed that the reaction products of acetaldehyde and some of its higher straight chain homologues with one equivalent of hydrazine are 3,6-dialkyl-hexahydro-1,2,4,5-tetrazines, which can be oxidized to the corresponding 3,6-dialkyl-1,2,4,5-tetrazines.

II. COMPUTER APPLICATION

The program used to develop the ESR spectra was originally written by W. M. Tolles for use with the CDC 1600 and IBM 360 series digital computers and associated plotting equipment. This system did not allow sufficient flexibility for repeated trial and error solutions of spectra. In order to assign a spectrum as complex as that generated (Figure 1), a great deal of trial and error technique was utilized. It was decided that a graphics display system where spectral parameters could be adjusted and immediately displayed would be ideal. As a result, the included program was written for the Xerox Data System 9300 digital computer and the Adage AGT 10 graphics display subsystem.

Use of this system allows minimum turn around time and valuable continuing train of thought. Two hundred graphic displays have been generated in a two hour time period. Once the graphics system has been initiated, the most complicated spectra consisting of up to 2000 lines are computed and displayed within twenty seconds.

The system has one major limitation, the ADAGE system has 2500 binary word core locations available when the "Gated" mode is used as in the included program. This is not an absolute figure, and changes as system modifications are incorporated. Thus, the system can be overloaded if the graphics and text arrays exceed approximately 2500 binary words (32 bits each).

The system as programmed allows one to calculate and display a first derivative ESR spectrum, to immediately integrate the spectrum, and to store the spectrum as a dashed line plot so that a second spectrum might be superimposed over the first for comparison purposes. The latter

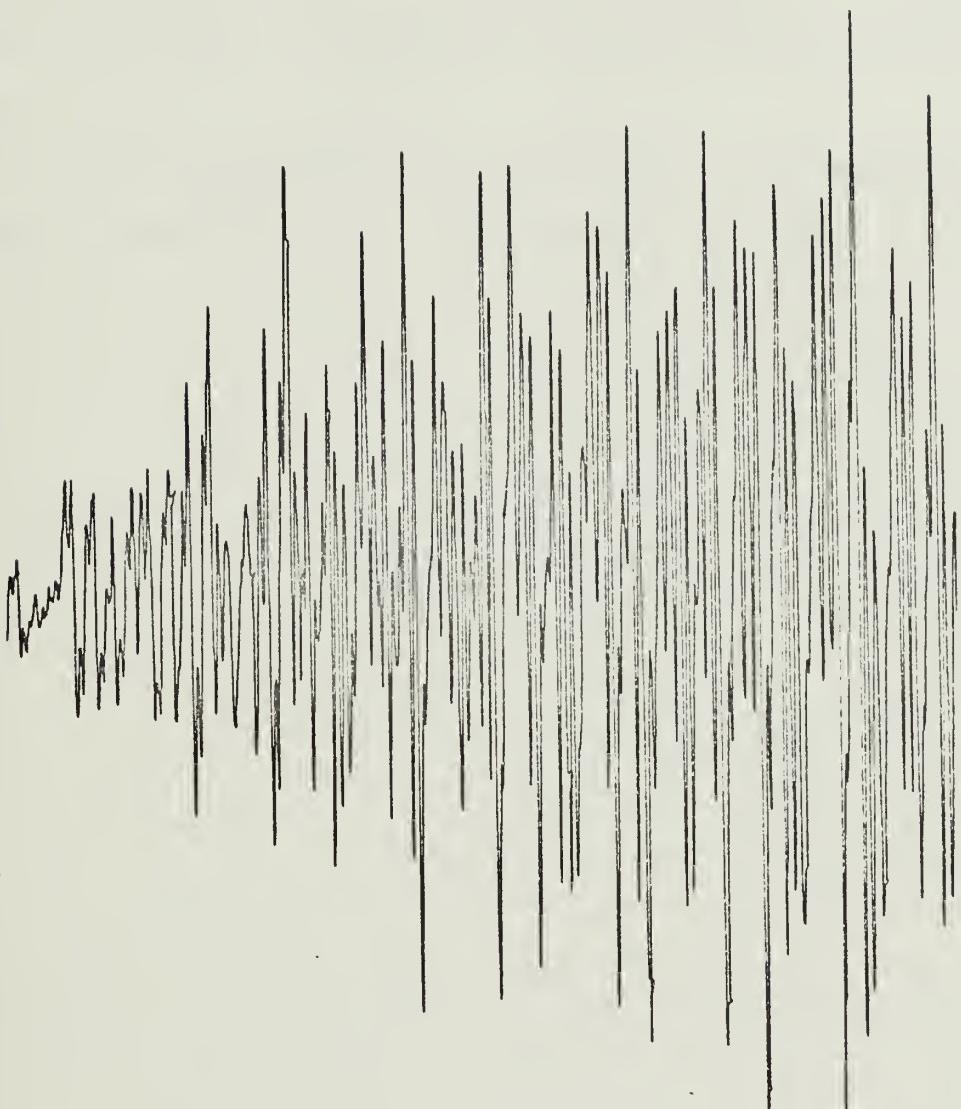


Figure 1: ESR signal of 1,5-Dimethylverdazyl in Dioxane
at 10°C. (first half)

L
B

10G

capability is extremely valuable when the user wants to see the effect of changing a parameter of a spectrum; one can display the original parameter as a dashed plot, and then display the new spectrum when a parameter or parameters changed slightly. One additional capability is included in the program, a spectrum can be constructed by adding together numerous other spectra.

The use of the program and an explanation of the parameters is included in Appendices A and B, and the program listing.

III. EXPERIMENTAL

A. ESR

The ESR spectrometer used was a Varian 4502-13 with Fieldial V-FR2503 magnetic field and a nine inch magnet using 100 KC modulation. The sample in a 4 mm open glass tube was placed in a standard reflection type cavity equipped with a Varian temperature control unit. A glass capillary attached to a nitrogen source via a needle valve was placed in the glass tube containing the sample and nitrogen was constantly bubbled through it. A nitrogen flow rate was maintained so that one could see the bubbling by shining a flashlight through the cavity glass port.

Solvents were chosen by trial and error. Dioxane was used because excellent resolution was obtained and radical lifetime was satisfactory. In addition, the spectrum immediately exhibited a repeated 1:2:1 multiplet indicative of a methylene group (Figures 1 and 2). Excellent results were also obtained using ethylether, chloroform (Figure 3), and diglyme (Figure 4). Satisfactory results were also obtained using acetonitrile, tetrahydrofuran, and acetone.

Spectra were obtained at various temperatures, and these temperatures were simply those that provided best resolution. In dioxane 10°C proved optimum, in diglyme 10°C, while in chloroform temperatures -60 to -40°C were ideal. Naturally, the lower the temperature, the longer the radical half-life.

The constant purging with nitrogen proved imperative for resolution. A spectrum of poor quality was immediately improved as the oxygen present was displaced by nitrogen.

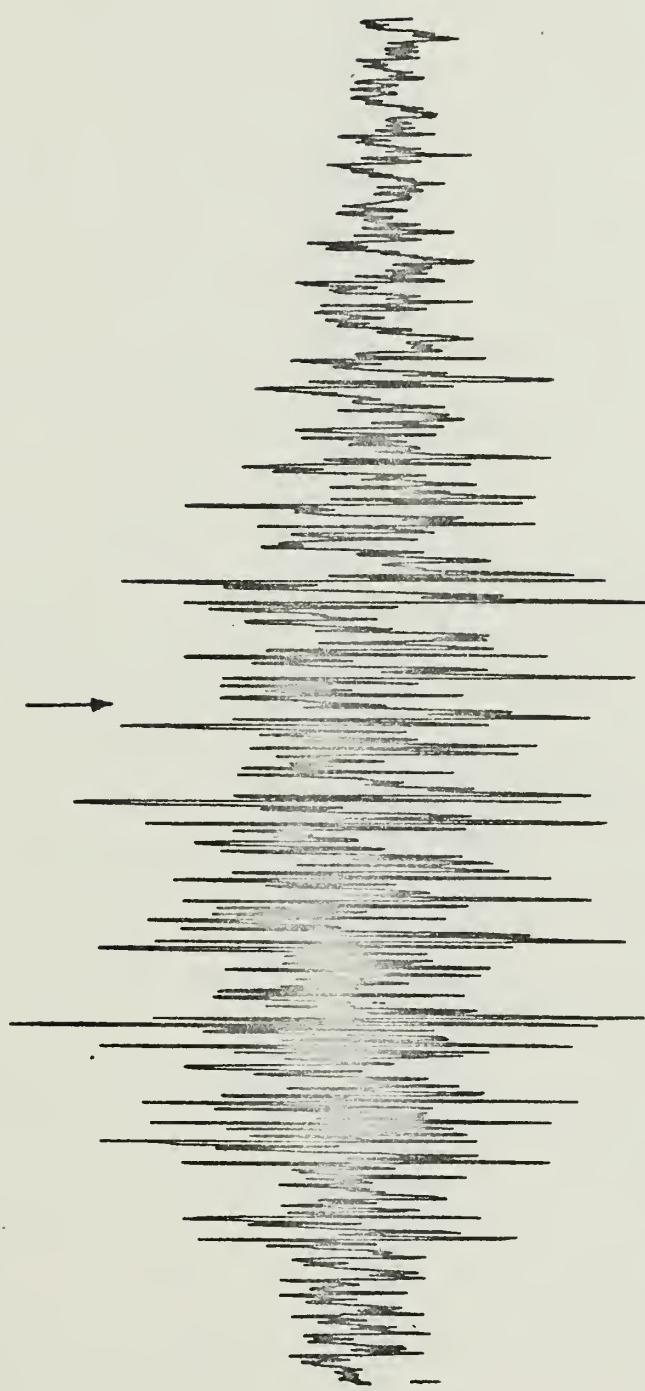
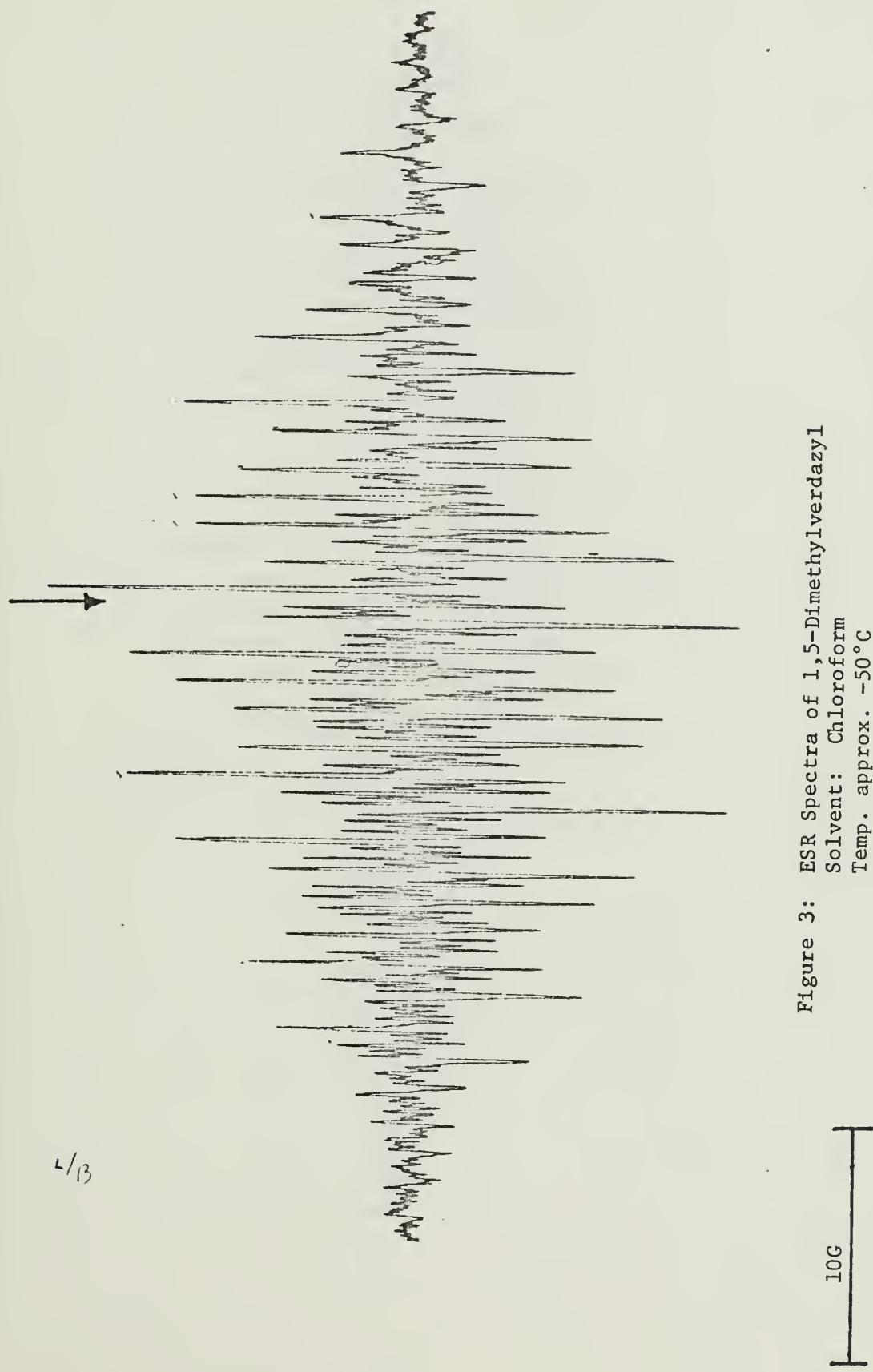
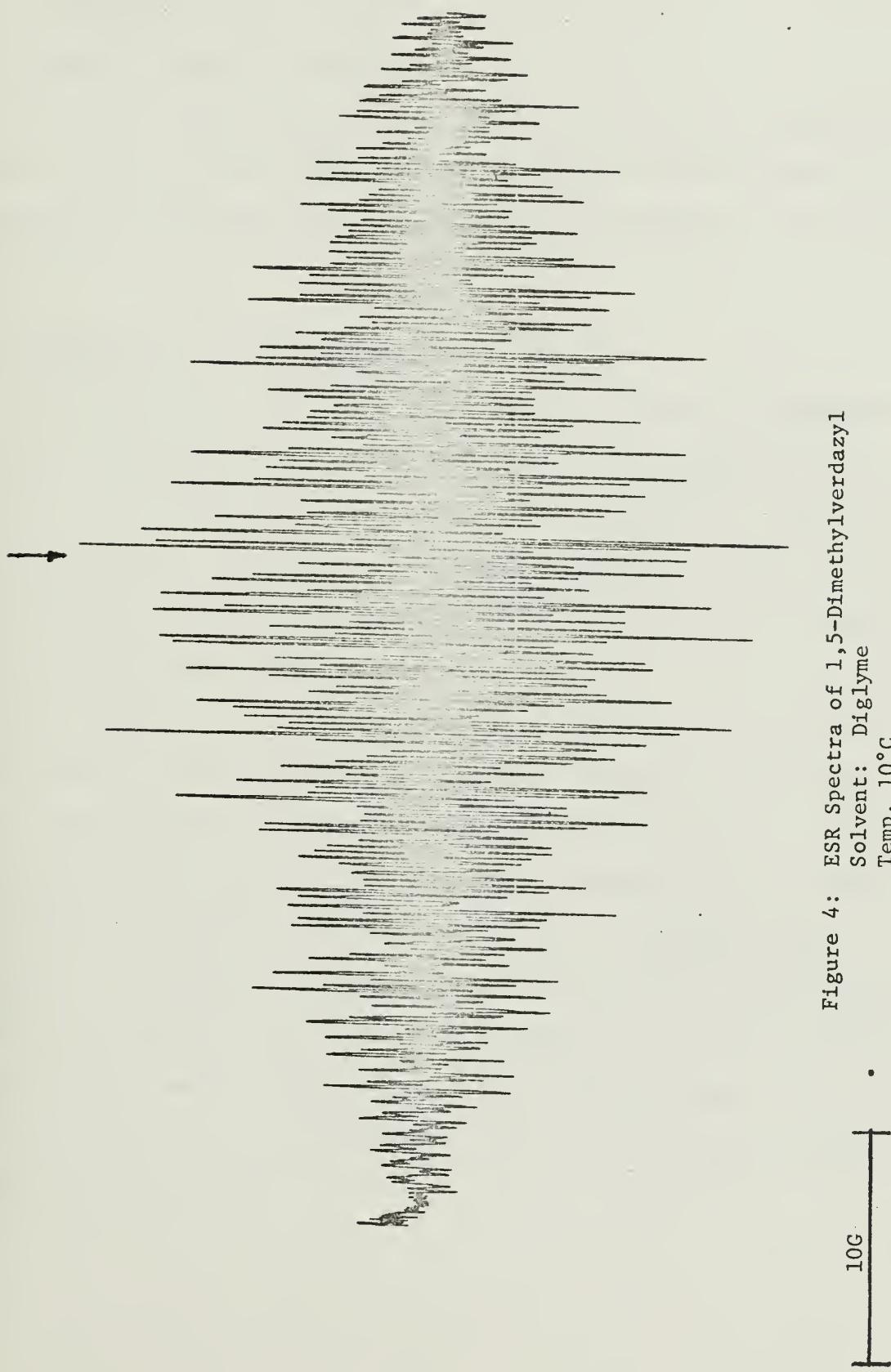


Figure 2: ESR Spectra of 1,5-Dimethylverdazyl
Solvent: Dioxane
Temp. 10°C

10G





Sample preparation was not quantitative. Enough hexahydro-s-tetrazine was dissolved in solvent (.5gm/50ml) to give a vivid violet color when HgO (1gm) was added with stirring.

Since the resulting spectrum was complex, it proved advantageous to spread it out on a strip chart recorder as Figures 1 and 19 attest. Spreading out the spectrum was a major step in assignment of this complex spectrum.

B. SYNTHESIS OF 1,4-DIMETHYLHEXAHYDRO-S-TETRAZINE

Formaldehyde (14.4ml 37%) is added dropwise to 10ml of methylhydrazine at room temperature while stirring over a period of approximately 0.5 hrs. After a period of time (1-2 hrs.), solid sodium hydroxide is added to the reaction mixture; crystals of 1,4 dimethyl-hexahydro-s-tetrazine precipitate from solution. After several minutes (not more than ten) the mixture is extracted with several fractions of ether (until just a few crystals adhere to the sodium hydroxide pellets). The ether solution is then evaporated to dryness in a rotary evaporator. The solid obtained is purified by recrystallization from n-hexane and carbon tetrachloride (10:1). Further purification was accomplished by fractional sublimation under a vacumn of 0.5-2.0 torr at 80-85°C. NMR analysis was used to determine sample purity. It was noted that the hexahydro-s-tetrazine that recrystallized from the n-hexane and carbontetrachloride wash after standing overnight, was on some occasions relatively pure. The radical precursor was noted in all preparations but appeared lesser in quantity when a slight excess of methylhydrazine was used.

C. CHROMATOGRAPHY

1. Thin Layer Chromatography

Aliquots of a saturated solution of 1,4-dimethyl-hexahydro-s-tetrazine were spotted on glass plates coated with a 1mm layer of Silica Gel-G. The samples were then eluted with a vertically ascending solvent (CH_3OH used, $(\text{CH}_3)_2\text{SO}$ and $\text{C}_2\text{H}_5\text{OH}$ suitable). The plates were then allowed to dry at room temperature. The chromatograms were developed by two different methods: a vapor of tetranitromethane was applied to the control surface; a spray of sodium nitrite was applied followed by a spray of .1N hydrochloric acid once the sodium nitrite had dried. The sodium nitrite treatment was preferred because of the strong oxidizing nature of TNM. After developing, the two areas containing the separated species were scraped off and washed repeatedly with a suitable solvent, usually CDCl_3 . An NMR analysis was then made to determine the species present. The method did not prove successful and was abandoned after numerous efforts.

2. Vapor Phase Chromatography

VPC (Figures 5, 6 and 7) was carried out on two instruments, the Bendix Series 2200 and the Aerograph Autoprep. Fair resolution was obtained using a fluorosilicone on teflon column (1/4in x 6-1/2ft, 11% Fluorosilicone FS 1265 on Teflon T6 - 30 mesh particles), column temperature 80-85°C, injection temperature 100°C, and detector temperature 150°C. An attempt was made to collect enough of each peak for an ESR measurement, but this was not successful. The peaks were collected by inserting an 8mm pyrex tube into the outlet port. The tube was passed through a dry ice packed styrofoam cup, and when a sample was needed the tube was warmed and washed with a suitable solvent into a container.

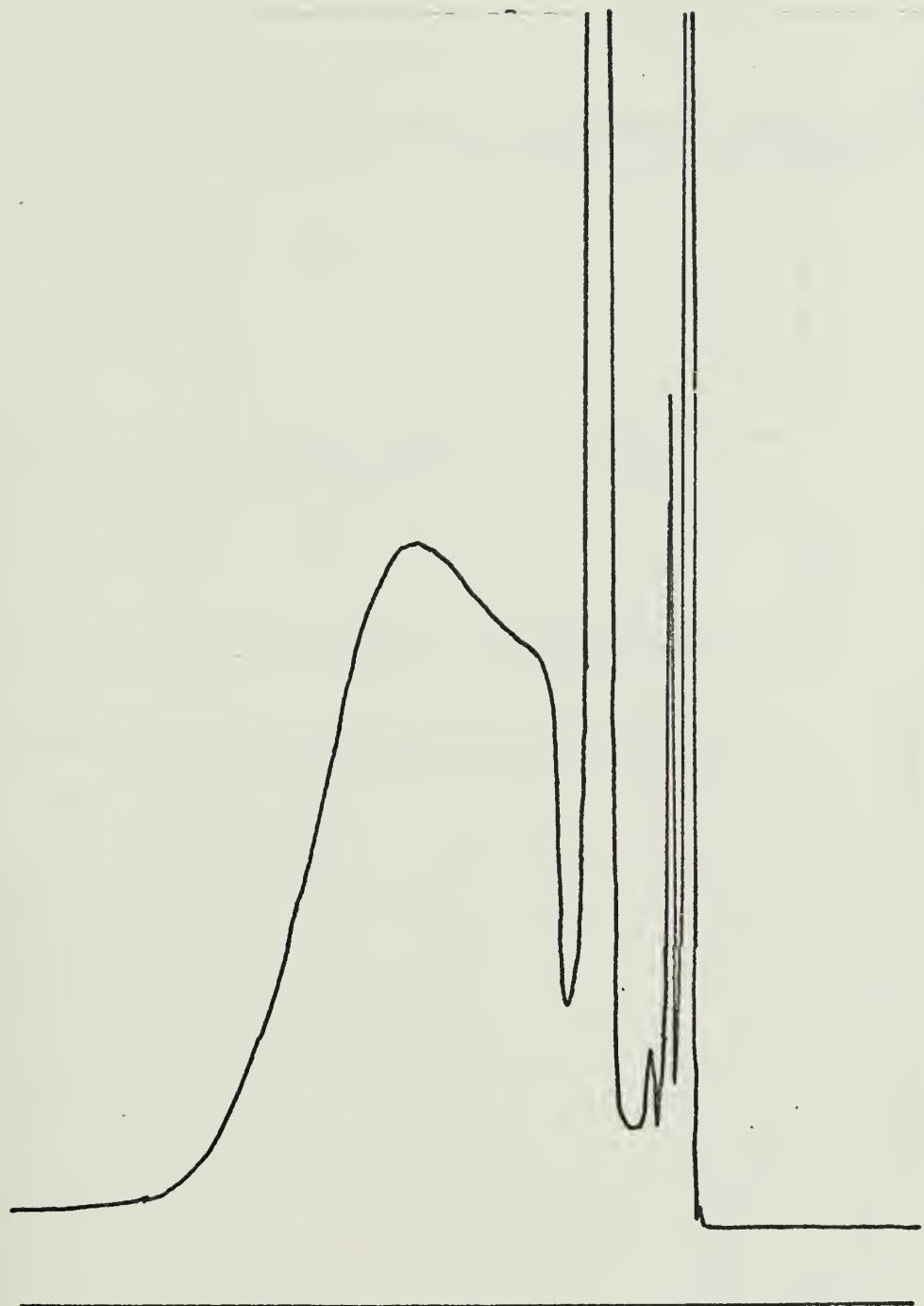


Figure 5: Gas Chromatogram of 1,4-Dimethyl-hexahydro-s-tetrazine
in Chloroform at 90°C (Bendix 2200)
(1/8 in. x 6-1/2 ft, 8% DC 200 on Teflon T6 - 30 mesh)
Speed = 1/2 in./min.

Figure 6: Gas Chromatogram of
1,4-Dimethylhexahydro-s-tetrazine
in Chloroform at 80°C (Bendix 2200)
(1/8 in. x 6-1/2 ft, 8% DC 200 on Teflon
T6 - 30 mesh)
Speed = 1/2 in./min.

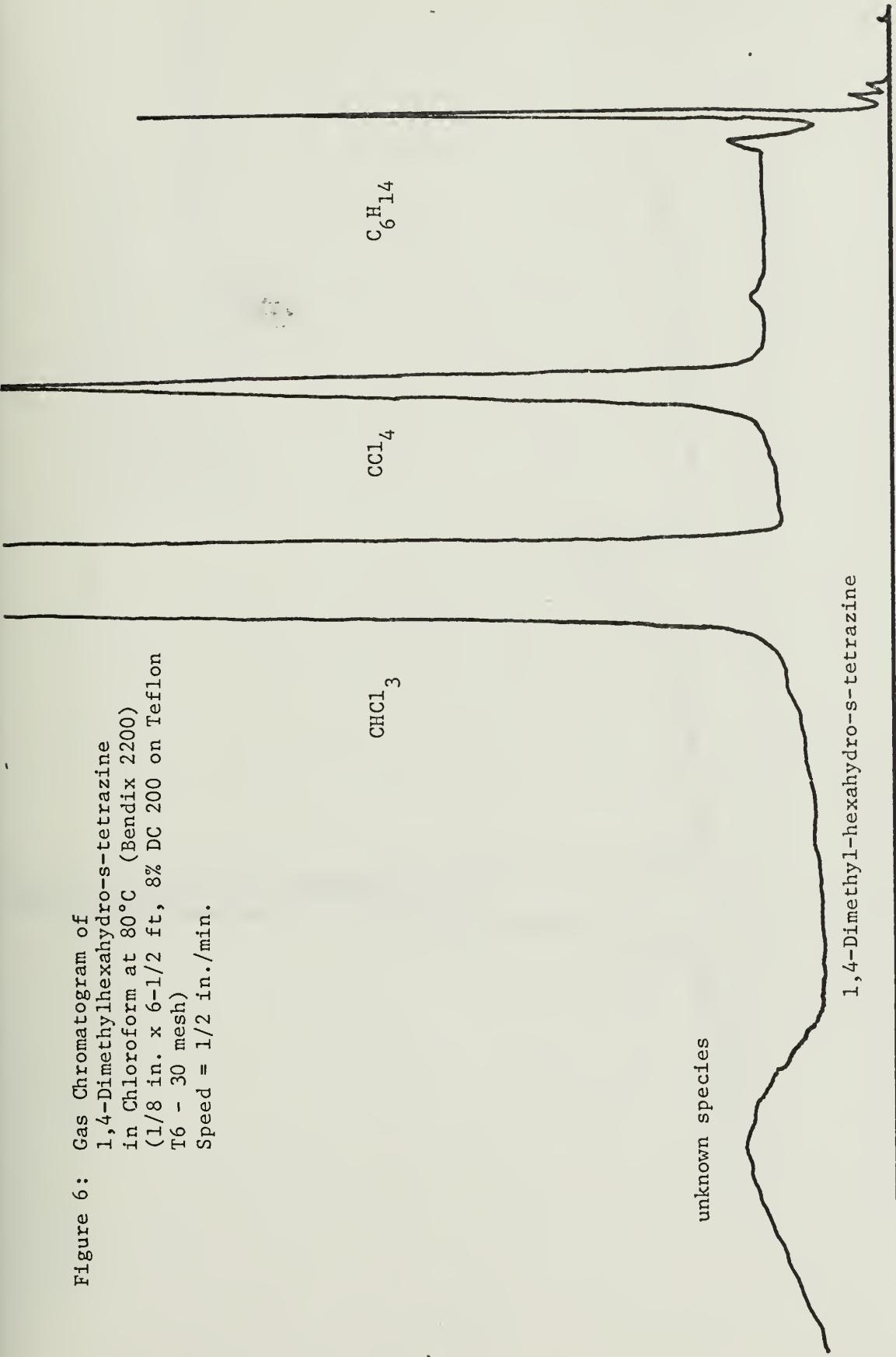
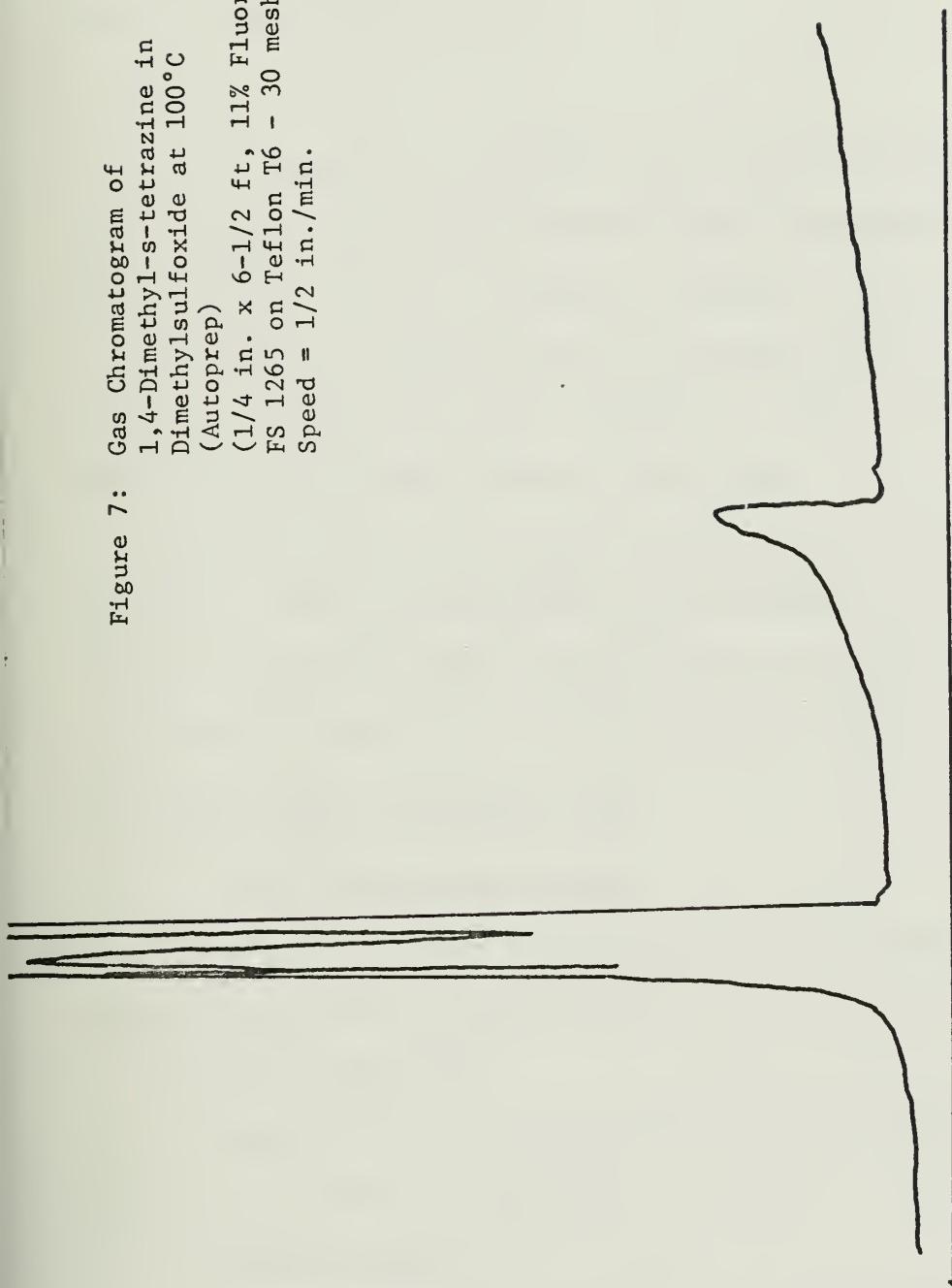


Figure 7: Gas Chromatogram of
1,4-Dimethyl-1-s-tetrazine in
Dimethylsulfoxide at 100°C
(Autoprep)
(1/4 in. x 6-1/2 ft, 11% Fluorosilicone
FS 1265 on Teflon T6 - 30 mesh particles)
Speed = 1/2 in./min.



Neither TLC nor VPC proved successful, and because of time limitations and immediate research goals, were abandoned. Each method should be further investigated in an attempt to separate the radical precursor and pure hexahydro-s-tetrazine.

D. NMR

Spectra were run on a Hitachi Perkin Elmer Model R-20A NMR Spectrometer equipped with a Model R-202VT Variable Temperature Equipment.

Spectra were observed in a temperature range of +34 to +145°C.

Solvents were chosen on a basis of boiling points, expense of deuterated species, and sample solubility. CDCl_3 , D_2O , and $(\text{CD}_3)_2\text{SO}$ with DSS or TMS as an internal reference were used.

Samples were not prepared quantitatively unless a UV correlation was to be run. Sample concentrations of approximately 0.2-0.3M hexahydro-s-tetrazine generally proved satisfactory for most spectra.

Results are discussed in Section IV and are tabulated in Table 1.

E. MISCELLANEOUS EXPERIMENTAL WORK.

1. UV and Visible Spectroscopy

Data were obtained from Beckman DK and DB series spectrometers.

Results are discussed in Section IV.

2. Mass Spectroscopy

Data were obtained from a CEC 21-103 Mass Spectrometer. The results are discussed in Section IV.

3. IR Spectroscopy

Spectrometer used was a Perkin Elmer 337. The results were similar to those discussed in Mashima's⁴ paper on tetraformaltriazine and Wiley⁶ et al's discussion of dimethylhydrazones of aliphatic aldehydes. They will not be further discussed.

IV. RESULTS AND DISCUSSION

A. NMR DATA AND INTERPRETATION

Table 1 presents the NMR data and data obtained from the literature. It can be seen that the assignments are consistent where they can be compared and in other cases within bounds expected when solvent differences are considered.

The most striking observation made during the course of this study is that the violet paramagnetic species referred to earlier, results only when HgO is added to hexahydro-s-tetrazine showing in addition to its own NMR peaks, some or all of the peaks listed under 1,5-dimethyl-hexahydro-s-tetrazine. Pure hexahydro-s-tetrazine with spectra as shown in Figures 8 and 12 did not yield the violet radical species when HgO was added, whereas samples with NMR spectra such as those in Figures 9 and 13 did. This phenomenon proved consistent and many hours were spent purifying 1,4-dimethyl-hexahydro-s-tetrazine only to find that upon addition of HgO no violet color was seen nor was an ESR signal detected. This evidence was sufficient for the conclusion that the radical generated was the result of the HgO oxidizing a reaction side product with NMR spectra as described in Table 1.

The ratio of integrated peak heights of the 1,5-dimethyl-hexahydro-s-tetrazine indicates a 6:2:2 ratio.

The side product behaved differently in various solvents, most notably D₂O and (CD₃)₂SO. In D₂O the precursor would grow in at room temperature as depicted in Figures 8 and 9, and if the same sample was exposed to air on a watch glass at room temperature the precursor would grow in just as it did in D₂O solution (compare Figures 8 and 9 which show the D₂O case with Figures 16 and 17 which show the air case).

Table 1: TABULATED NMR DATA

D_2^0 (DSS)	D_2^0 (DSS)	$CDCl_3$ (TMS)	DMSO (TMS)
1,4-Dimethyl-hexahydro-s-tetrazine "Dimer"	Exp. 7.65(s,6H) 6.36(s,4H)	Exp. 7.62(s,6H) 6.43(s,4H) 7.3 (s,2H)	Exp. 7.8(s,6H) 6.6(s,4H)
Formaldehyde methylhydrazone "Momomer"	Exp. 7.32(s,3H) 3.48 AB quartet 3.68	Lit. 7.65(s,6H) 6.43(s,4H) 7.3 (s,2H)	Exp. 7.38(s,3H) 3.82 AB quartet 4.02
(in acetone d_6) ¹⁷	Lit. * 7.28(d,3H) 3.67 AB quartet 4.09		
1,5-Dimethylhexahydro-s-tetrazine "Precursor"	Exp. 7.58(s,6H) 6.72 6.06	Exp. 7.56(s,6H) 6.83 6.98	Exp. 7.75(s,6H) 6.91 6.31

*Reported addition of H_2O caused doublet to coalesce.

Figure 8: NMR Spectrum of 1,4-Dimethyl-hexahydro-s-tetrazine
in D₂O at 38°C (pure)

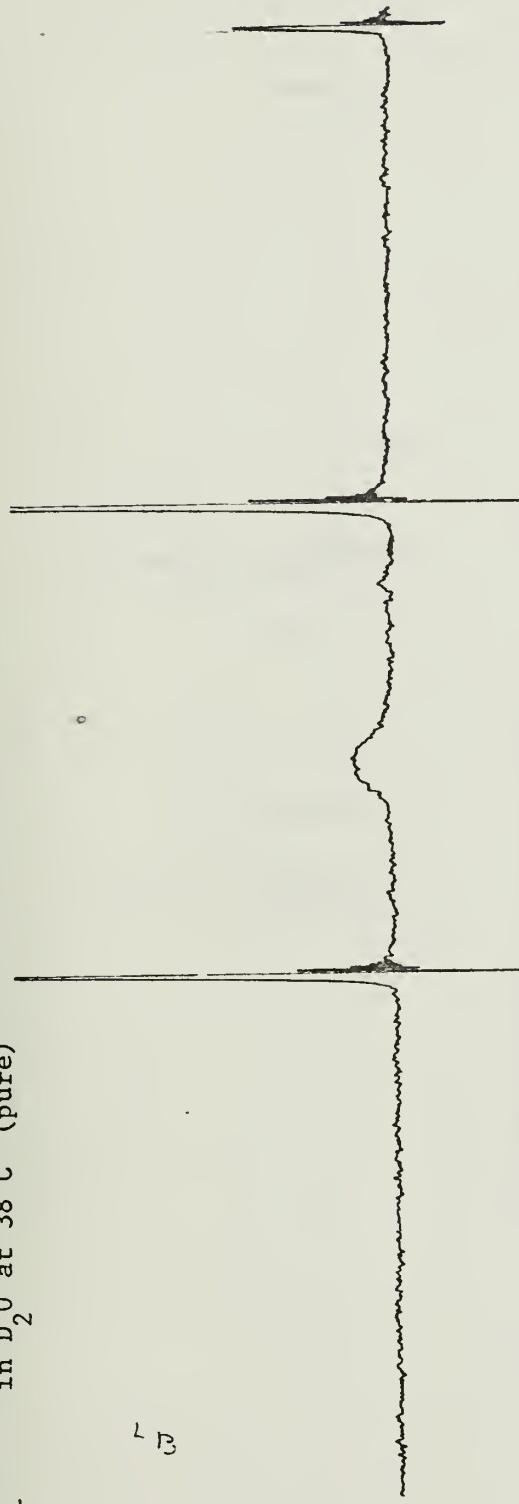


Figure 9: NMR Spectrum of 1,4-Dimethyl-hexahydro-s-tetrazine
in D₂O at 38°C (impure)

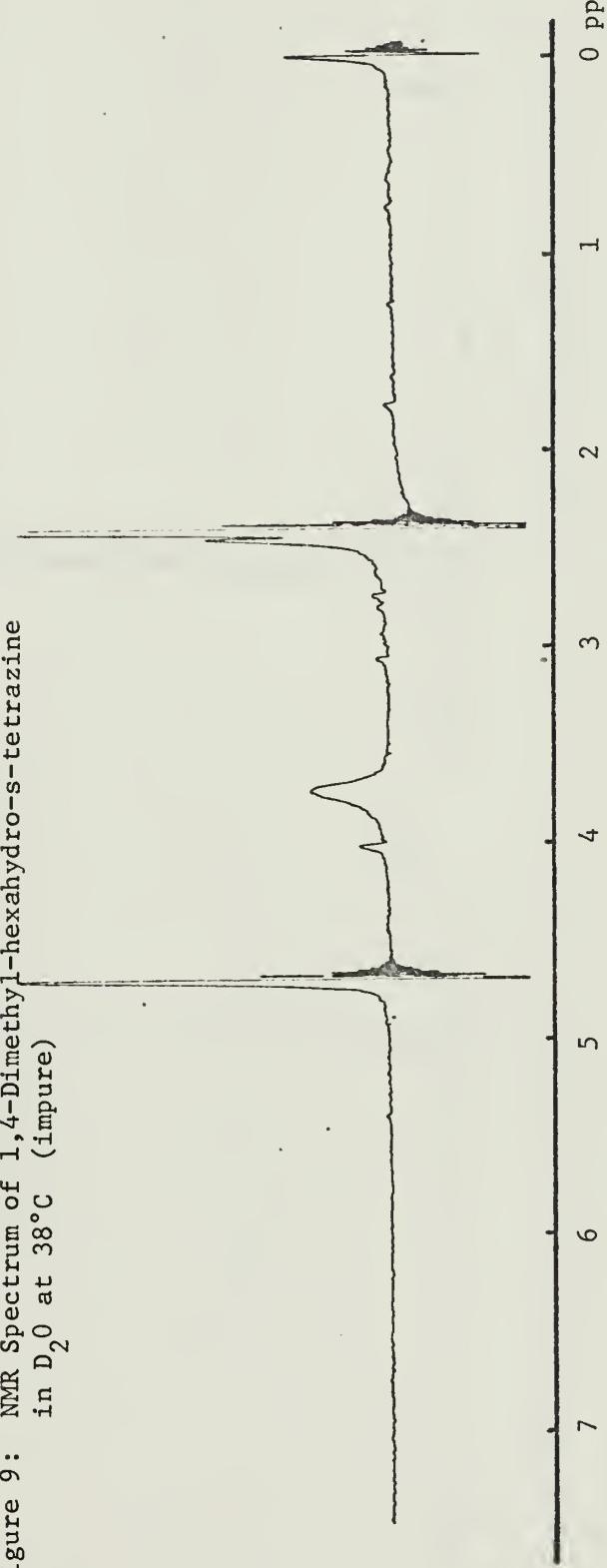


Figure 10: NMR Spectrum of
1,4-Dimethyl-hexahydro-s-tetrazine
in D₂O at 90°C

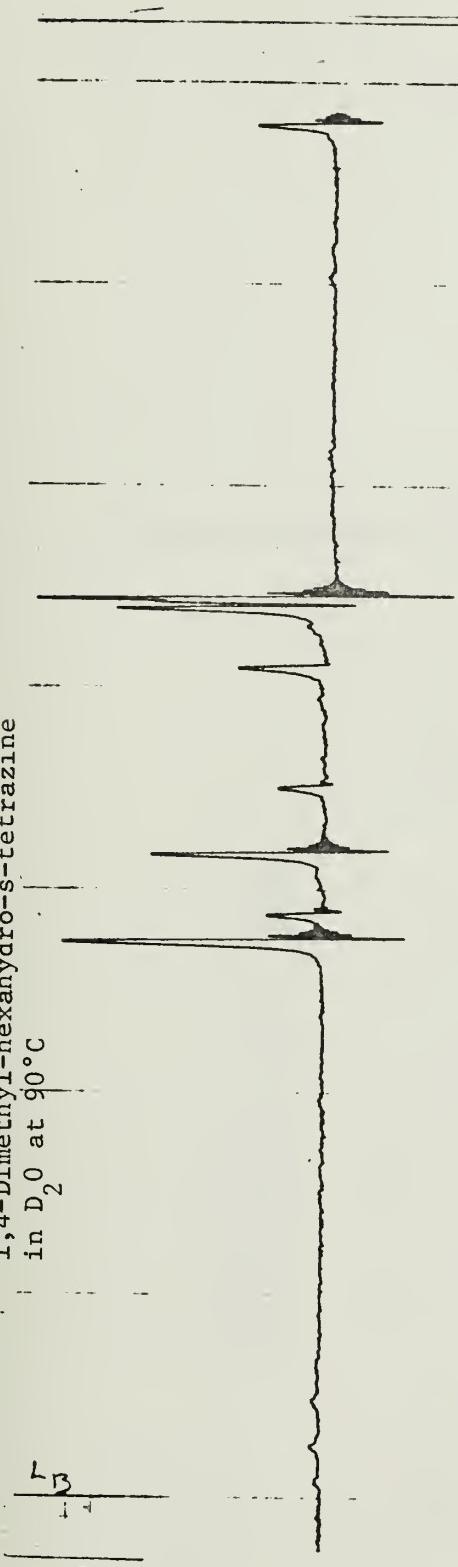
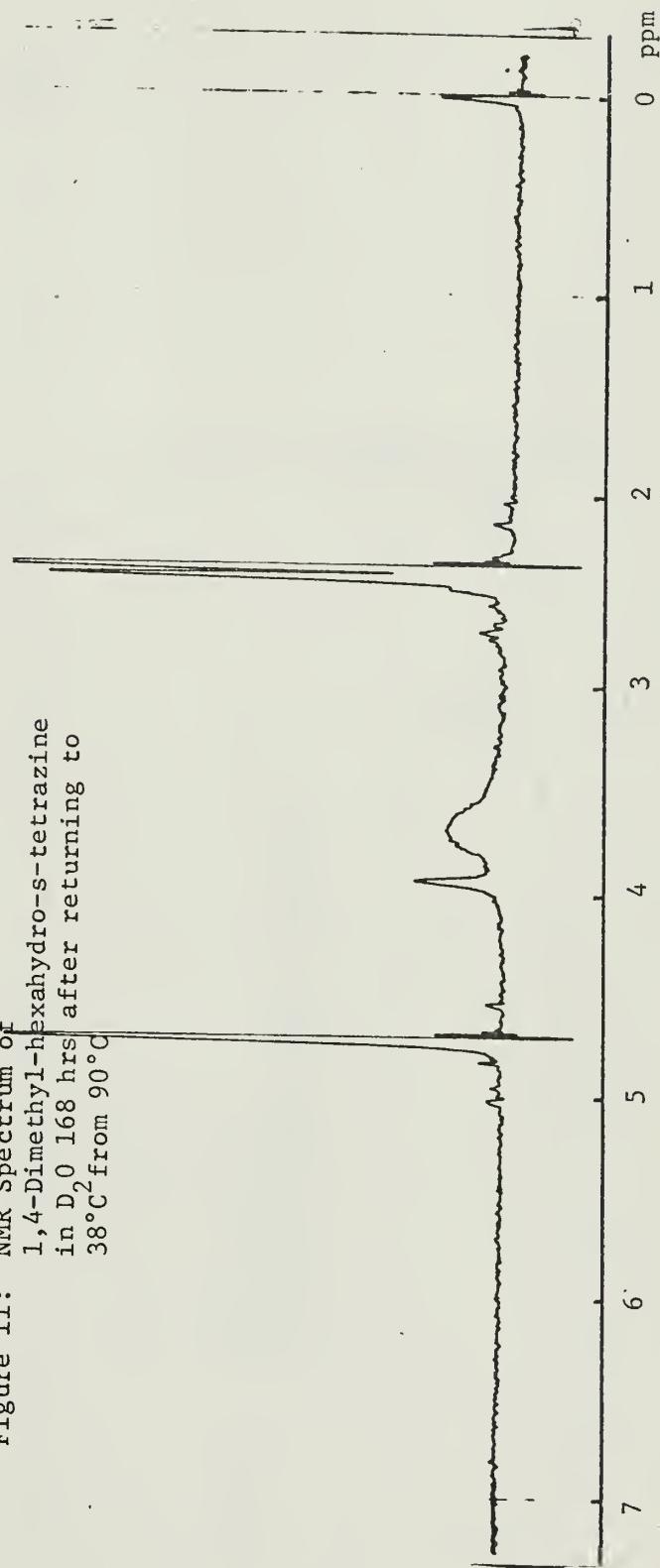


Figure 11: NMR Spectrum of
1,4-Dimethyl-hexahydro-s-tetrazine
in D₂O 168 hrs after returning to
38°C from 90°C



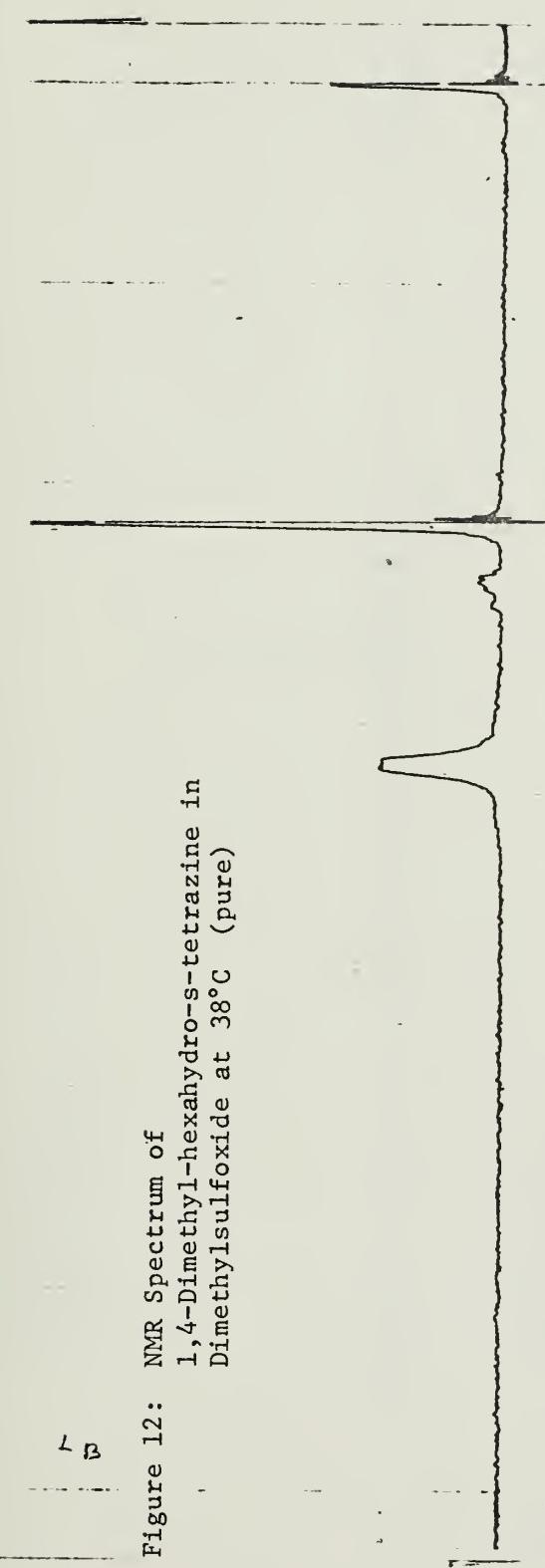


Figure 12: NMR Spectrum of
1,4-Dimethyl-hexahydro-s-tetrazine in
Dimethylsulfoxide at 38°C (pure)

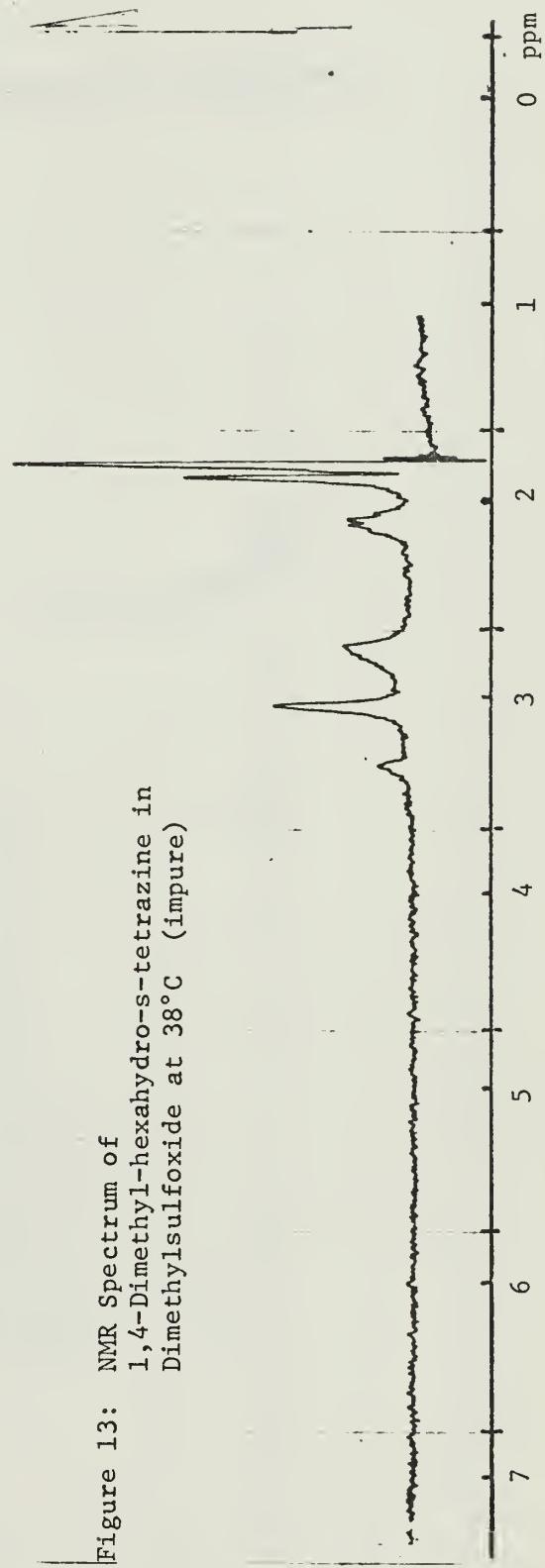


Figure 13: NMR Spectrum of
1,4-Dimethyl-hexahydro-s-tetrazine in
Dimethylsulfoxide at 38°C (impure)

7

Figure 14: NMR Spectrum of
1,4-Dimethyl-hexahydro-s-tetrazine in
Dimethylsulfoxide at 140°C

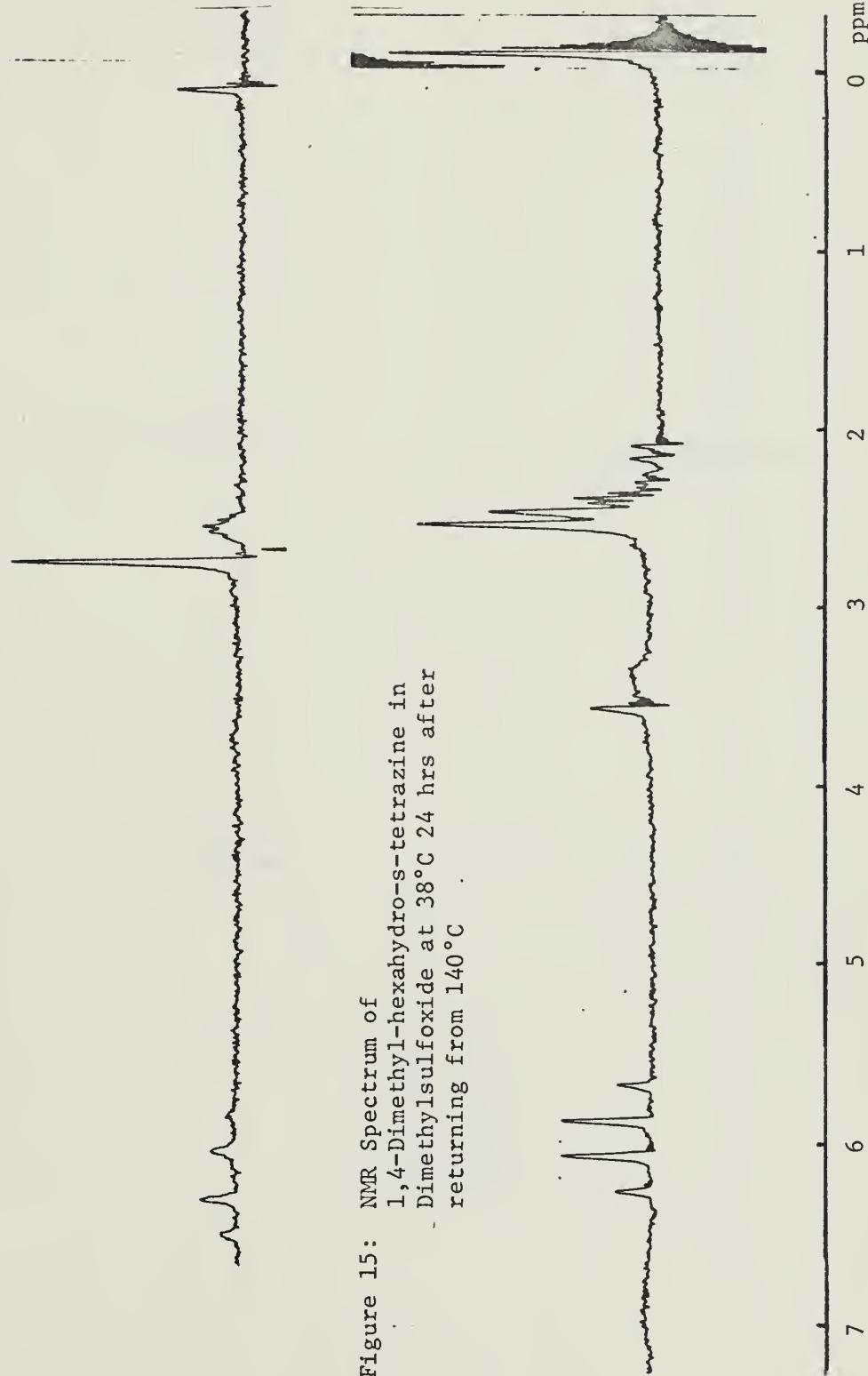
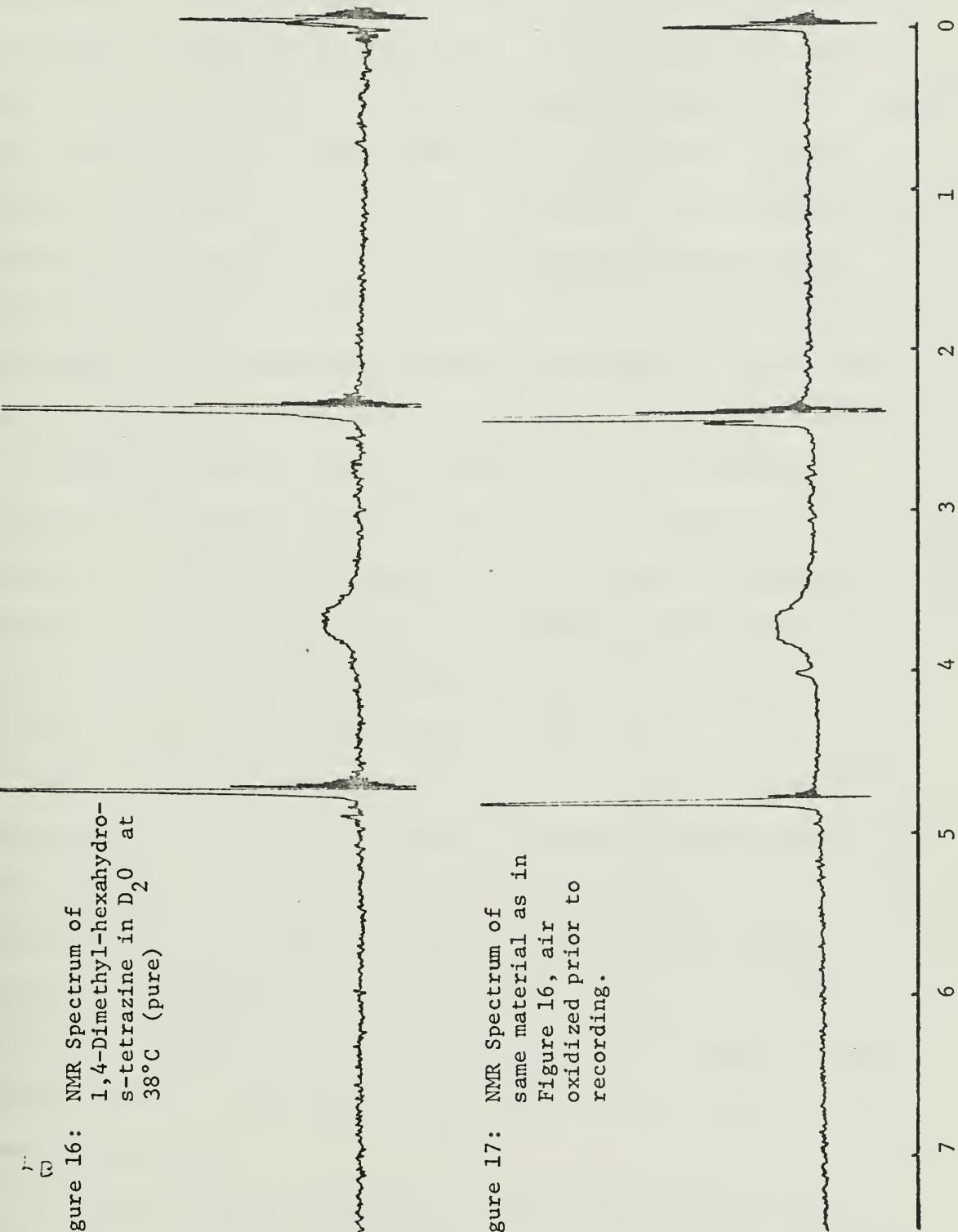


Figure 15: NMR Spectrum of
1,4-Dimethyl-hexahydro-s-tetrazine in
Dimethylsulfoxide at 38°C 24 hrs after
returning from 140°C



As the temperature of a D_2O solution of 1,4-dimethyl-hexahydro-s-tetrazine was raised the monomer (formaldehyde methylhydrozone) and the 1,5-dimethyl species grew in (Figure 10): it appears that the monomerization process then gives rise to the 1,5-dimethyl species. It was thought that a true equilibrium existed between the three species, the dimer, monomer, and precursor; and in order to verify this a D_2O solution of pure hexahydro-s-tetrazine was subjected to a complete temperature cycle (38°C to 90°C and reverse) NMR analysis. The precursor was evident in the formerly pure material at 38°C and it appears that the same amount was present 168 hours later at this same temperature (Figures 8 and 11).

A somewhat different situation exists in $(CD_3)_2SO$, the monomer appeared at approximately 50°C and was in evidence before the 1,5-dimethyl-hexahydro-s-tetrazine, or precursor. At 90°C the spectrum showed primarily monomer but some precursor, at 140°C all monomer existed (Figure 14). After a sample in $(CD_3)_2SO$ was elevated to 140°C and returned to 38°C, all three species were present as shown by Figure 15.

The above data is consistent with the results reported by Haven⁸ concerning the stability of the dimer of heptanal methylhydrazone; the dimer of heptanal methylhydrazone is extremely unstable to heat and rapidly monomerizes in polar solvents. He submits that the dimer of heptanal methylhydrazone is not a six membered ring (1,4-dimethyl-3,6-dihexylhexahydro-s-tetrazine), but more probably a four membered ring. He also argues that six-membered ring formation would be limited to monomethylhydrazones.

An attempt was made to perform a UV/NMR correlation experiment, as the precursor grew in or faded out on the NMR, spectrometer parallel UV measurements were made. Unfortunately, no consistent results were obtained.

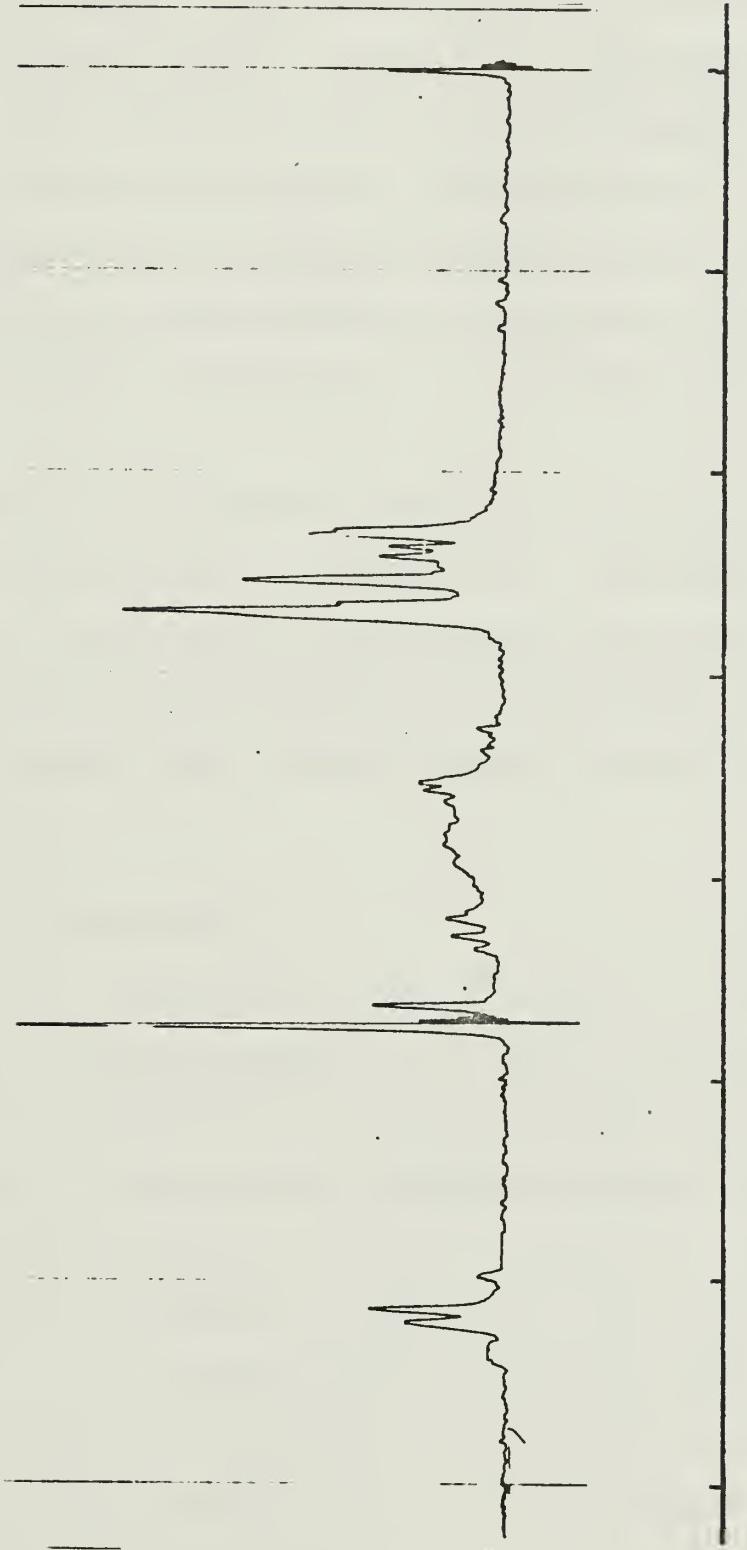


Figure 18: NMR Spectrum of 1,4-Dimethylhexahydro-s-tetrazine plus others in D₂O resulting from a preparation using excess Formaldehyde. Temp. 38°C

L_B

Two absorption peaks were noted in the NMR spectrum which were assigned to pure hexahydro-s-tetrazine; a peak corresponding to the reported¹⁷ formaldehyde methylhydrazone at 233 nm. accompanied by a second weaker peak at 315 nm. were noticed. The latter peak has not been assigned but may be the result of a hydrazone rearrangement, possibly an azine.

An NMR analysis of pure 1,4-dimethyl-hexahydro-s-tetrazine oxidized to 1,4-dimethyl-dihydro-s-tetrazine showed peaks indicative of the hexahydro, tetrahydro, and dihydro-s-tetrazines but no 1,5-dimethyl-hexahydro-s-tetrazine.

An examination of the hexahydro-s-tetrazine prepared by using varying amounts of formaldehyde showed a marked difference. When formaldehyde was short, the product showed relatively small amounts of the radical precursor; when it was in excess, the NMR spectrum (Figure 18) showed a relatively large amount of monomer, dimer, and some precursor plus some other minor products or product.

B. ESR DATA AND INTERPRETATION

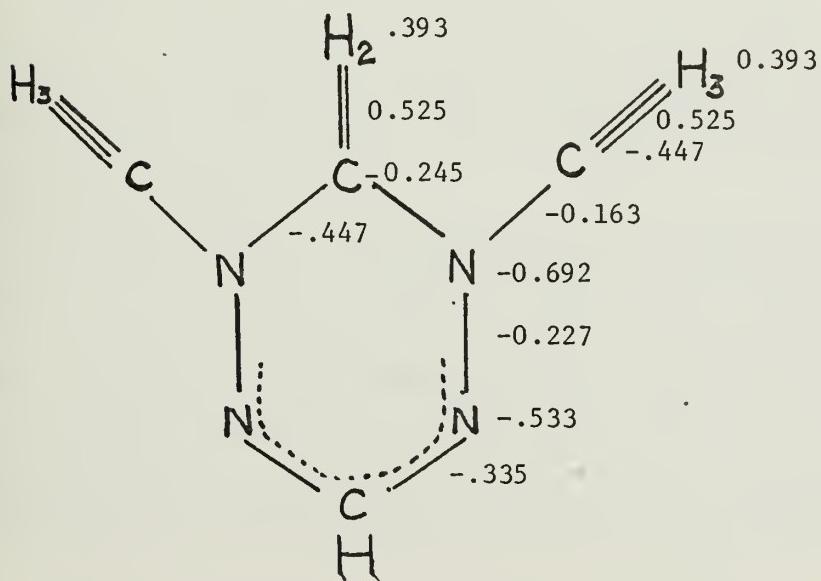
As one can see by examination of Figures 1 through 4, the ESR spectra generated are very complex regardless of the solvent or temperature chosen. Experimentally assigned and calculated coupling constants are presented in Table 2. The calculated constants were obtained from a basic molecular orbital calculation offered by Tolles et al¹. These values are based on the relation $a^n = Q_N^{n\beta}$ where Q_N^n has a value of -26.8 and $Q_{NCH_3}^H = 25.4$. The correlation between calculated and experimental values is good considering the approximations inherent in the application of the molecular orbital parameters calculated for 1,4-dihydro-s-tetrazine cation radicals to 1,5-dimethyl-verdazyl.

Table 2: COUPLING CONSTANTS AND MOLECULAR ORBITAL PARAMETERS

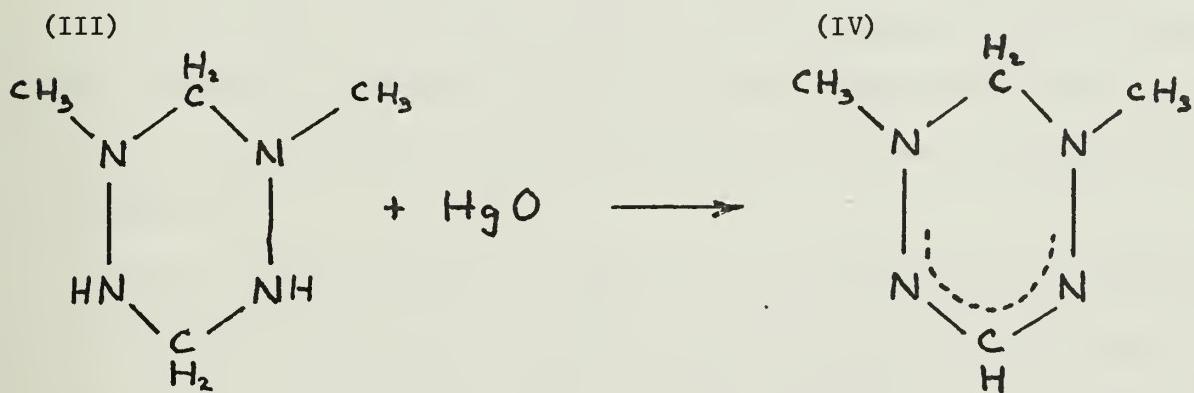
Coupling Constant, Gauss			
Calculated	Experimental	Experimental	Accident
$a_{N_1} = 4.32$	5.96		5.96
$a_{N_2} = 8.66$	11.4		3.9
$a_{CH_3} = 4.09$	3.9		11.4
$a_H = 0.0$	1.06		1.06
$a_{2H} = 0.0$.39		.39

Molecular orbital parameters for 1,5-Dimethyl-verdazyl.

The number adjacent to an atom represents the self consistent colomb integral for that atom, and that adjacent to a bond represents the resonance integral between the two atoms.¹



At this point, it is appropriate to justify the assignment of the precursor discussed in the NMR section as 1,5-dimethyl-hexahydro-s-tetrazine and now the assignment of the radical itself as 1,5-dimethyl-verdazyl. Two facts are most important: the 6:2:2 NMR integrated peak height ratio and the atomic groupings making up the assigned spectrum. Although further discussion will be presented on this subject, the calculated spectrum that best fit the experimental spectrum was found to be the result of the electron spin resonance contributions of two different pairs of equivalent nitrogens, one pair of equivalent hydrogens, a lone hydrogen, and six other equivalent hydrogens. In view of the NMR spectrum a structure consistent with III is proposed and upon treatment with HgO, structure IV is theorized.



Structure (IV) is in accord with the structure proposed by Kuhn and Trischmann¹⁹ for verdazyls.

Carrington²¹ describes the problem of determining the splitting constants from observed spectra as intelligent guesswork, or trial and error. He mentions that complex spectra with lines overlapping resulting in distorted intensities may necessarily have to be reconstructed although detailed examination of the wings will usually prove profitable

in assignment. In consideration of this observation consider spectra 20 and 21; they arise from "accidents" in assignment which are to be fully discussed.

Literature examined on aromatic substituted verdazyls (literature on aliphatic substituted verdazyls not available) indicates the four nitrogens have equivalent or nearly equivalent coupling constants. The spectrum shown by Figure 20 is the result of atomic groupings $a_N = 11.39$, $a_{2NH} = 5.96$, $a_{CH_3} = 3.93$, $a_{2H} = .33$, $a_H = 1.05$, and $a_H = 29.7$. This is theoretically highly improbable because of the large single H coupling constant (29.07), and any attempt to formulate a structure containing such groupings proved impossible. This does show that strictly fitting the experimental spectrum with a calculated spectrum has inherent shortcomings.

The spectrum represented by Figure 21 is an altogether different case; it is theoretically feasible but the calculated spectrum does not fit the observed spectrum in the wings when compared to the fit of the spectrum in Figure 19.

In this case the coupling constants are the same but they are assigned to different atomic groups ($a_{N1} = 5.96$, $a_{N2} = 3.9$, $a_{CH_3} = 11.4$, $a_H = 1.06$ and $a_{2H} = .39$). Ironically, although this is the poorest fitting calculated spectrum it agrees with the theoretical value of coupling constants promulgated by Neugebauer²²; Fischer²³; Neugebauer and Russell²⁴, Neugebauer and Trischmann and Targel²⁵; Kuhn and Trischmann¹⁸. They all have reported on aromatic substituted verdazyls and report four equivalent nitrogen coupling constants. Primarily, the nitrogens were assigned nearly equivalent coupling constants because of experimental evidence of nine broad lines (which by basic ESR theory is associated with four nearly identical nitrogen atom spin densities) of intensity 1:4:10:16:19:16:10:4:1.

Figure 19 - 1A

Experimental ESR Spectrum of 1,5-Dimethyl-verdazyl, same Spectrum as that shown in Figure 1 but spread out on strip chart recorder



Figure 19 - 1B

Calculated ESR Spectrum of 1,5-Dimethyl-verdazyl (best match)

5G

Figure 19 - 2A
(continuation)

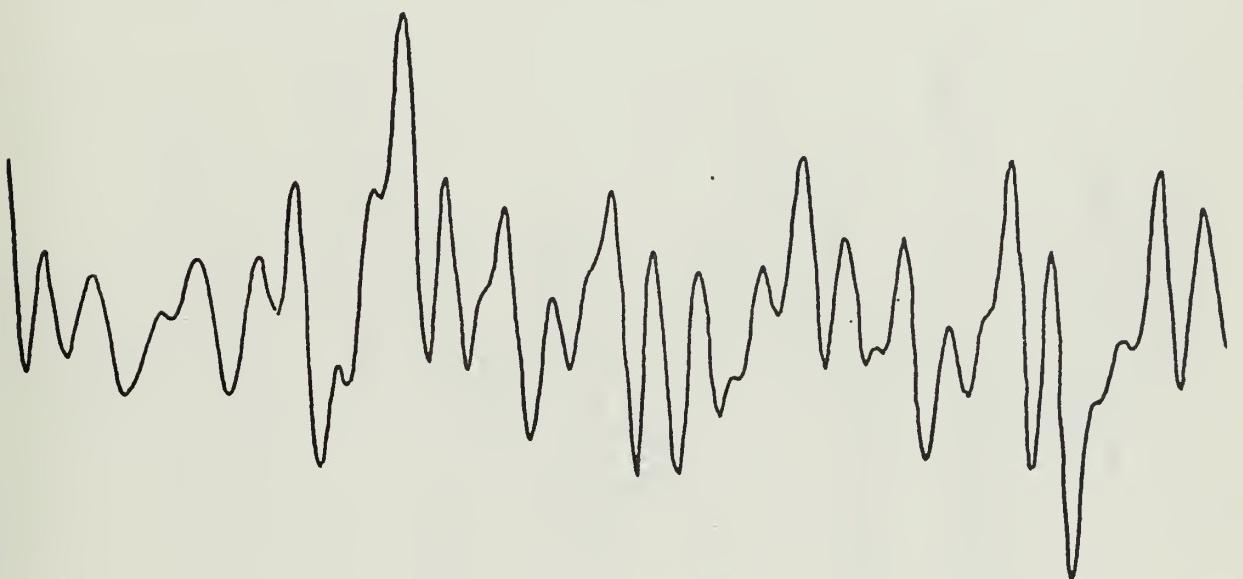
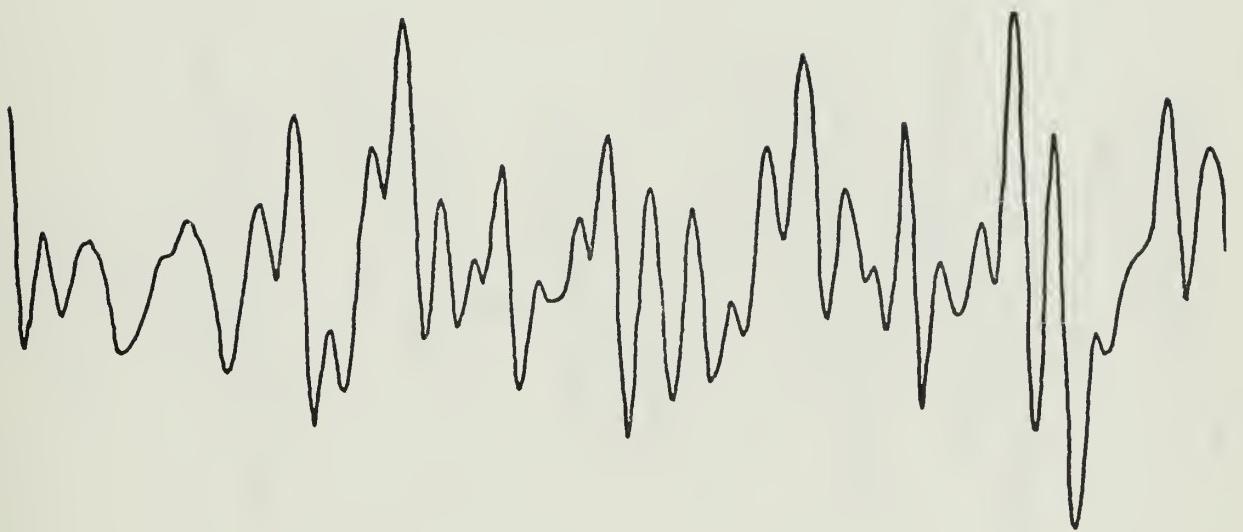


Figure 19 - 2B
(continuation)

5G

Figure 19 - 3A
(continuation)

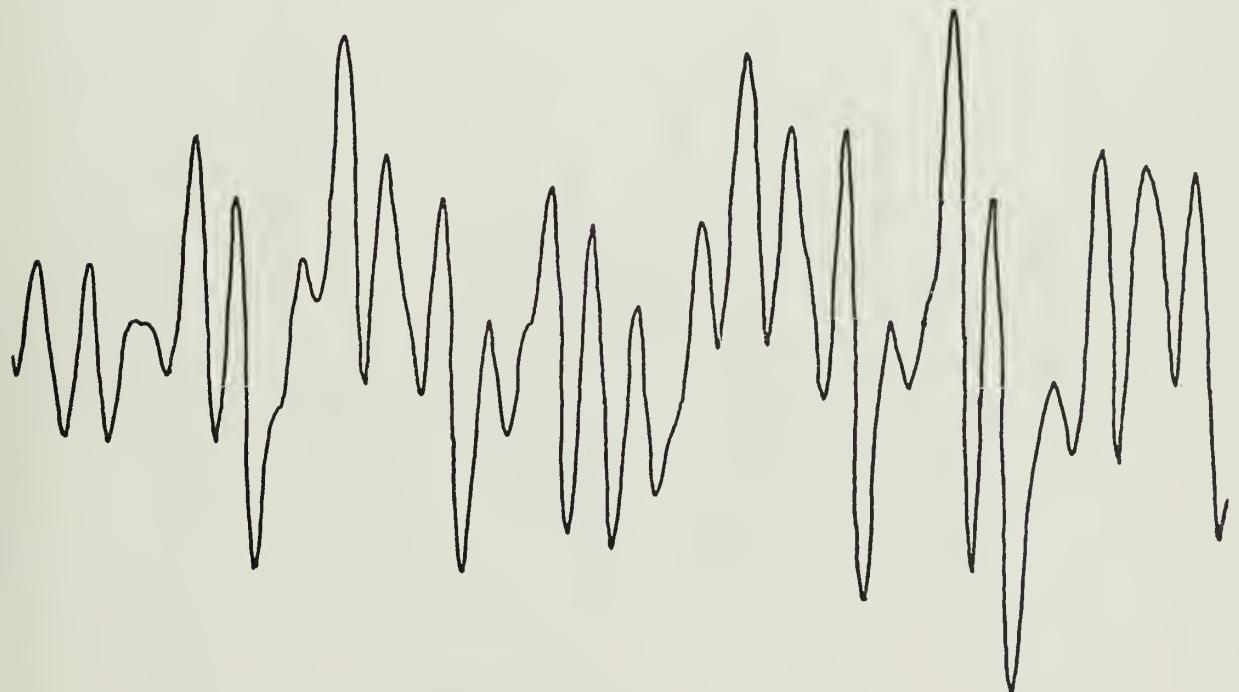


Figure 19 - 3B
(continuation)
5G



Figure 19 - 4A
(continuation)

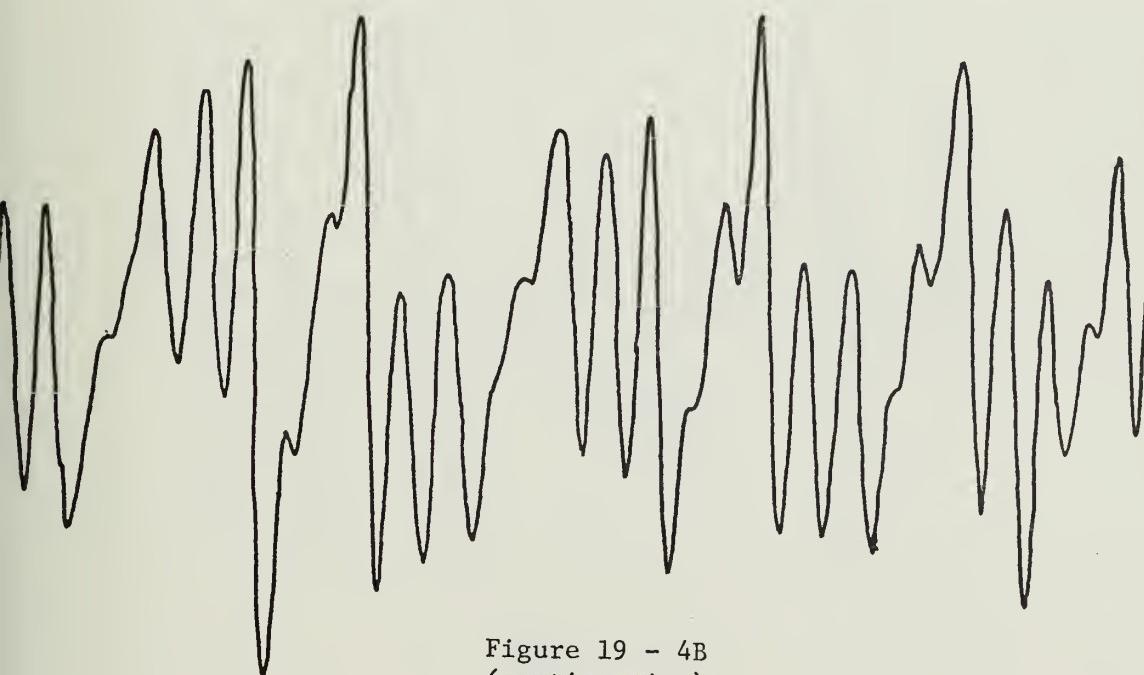
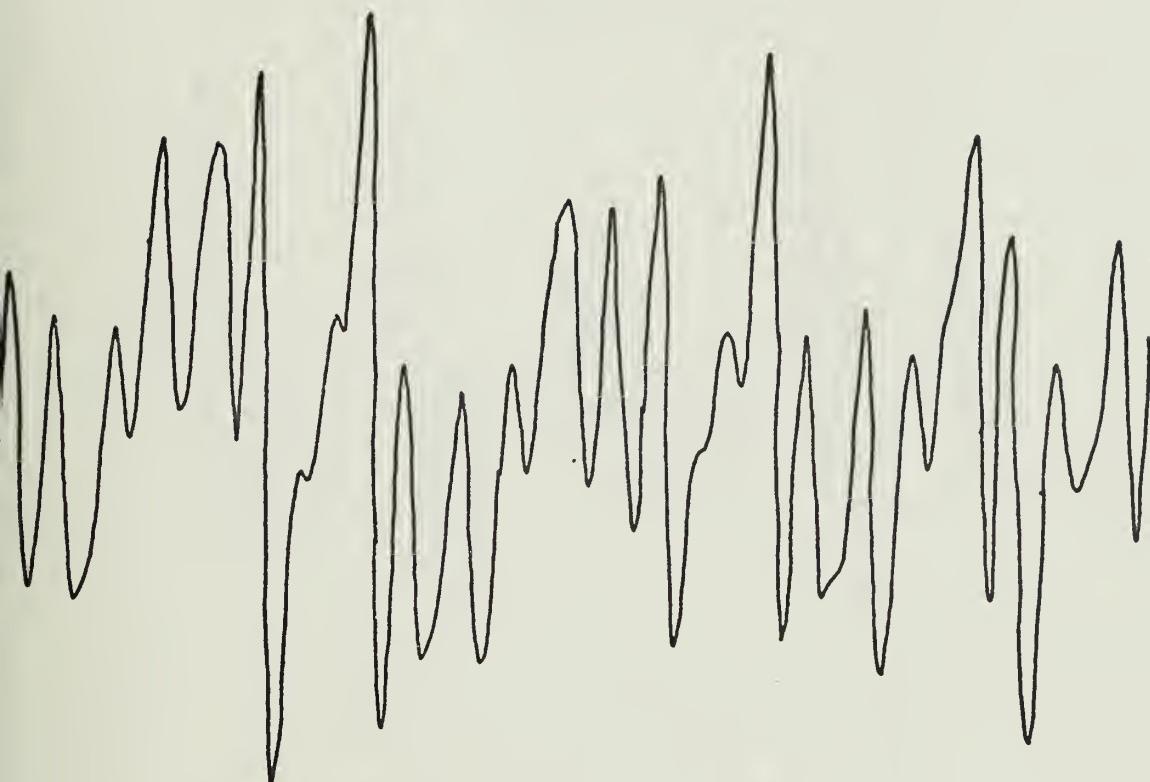


Figure 19 - 4B
(continuation)

5G

Figure 19 - 5A
(continuation)

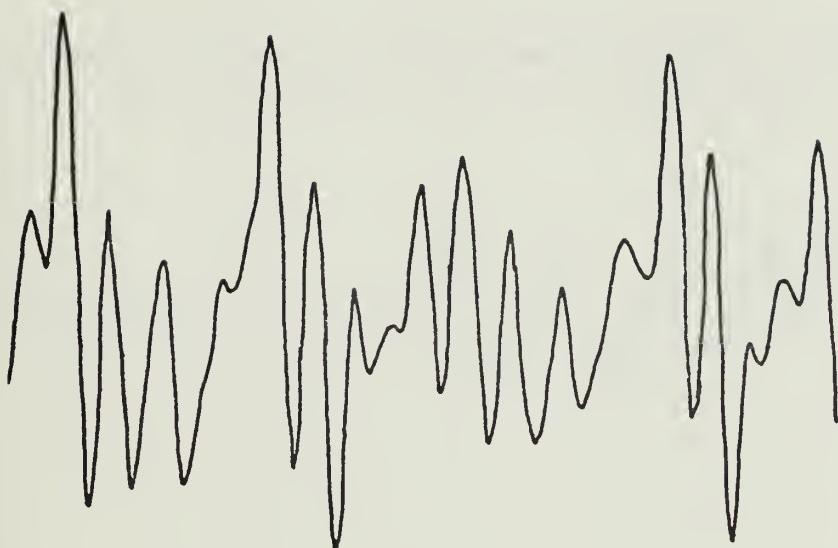


Figure 19 - 5B
(continuation)

5G



Figure 20 - 1A

Experimental ESR Spectrum of 1,5-Dimethyl-verdazyl, same Spectrum as that shown in Figure 1 but spread out on strip chart recorder

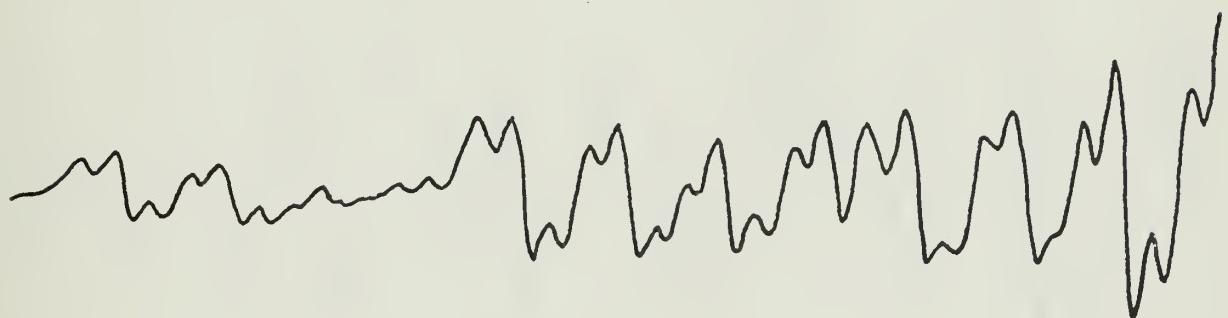


Figure 20 - 1B

Highly unlikely accidental calculated spectrum that matches exp. spectrum fairly well but is physically impossible.

5G

[-----]

Figure 20 - 2A
(continuation)

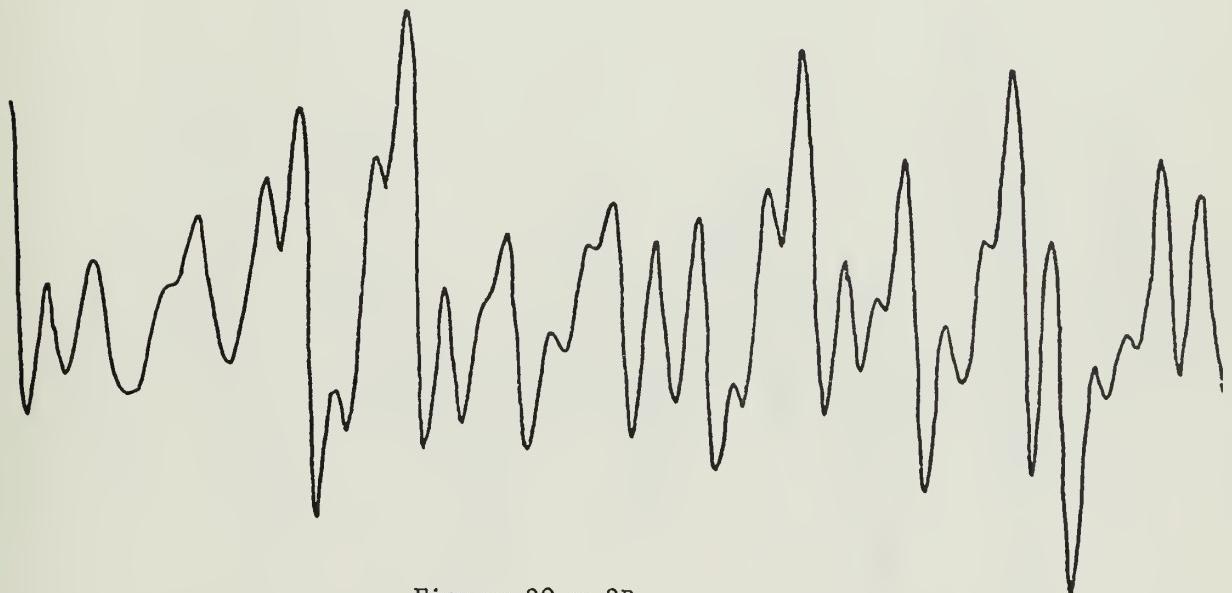
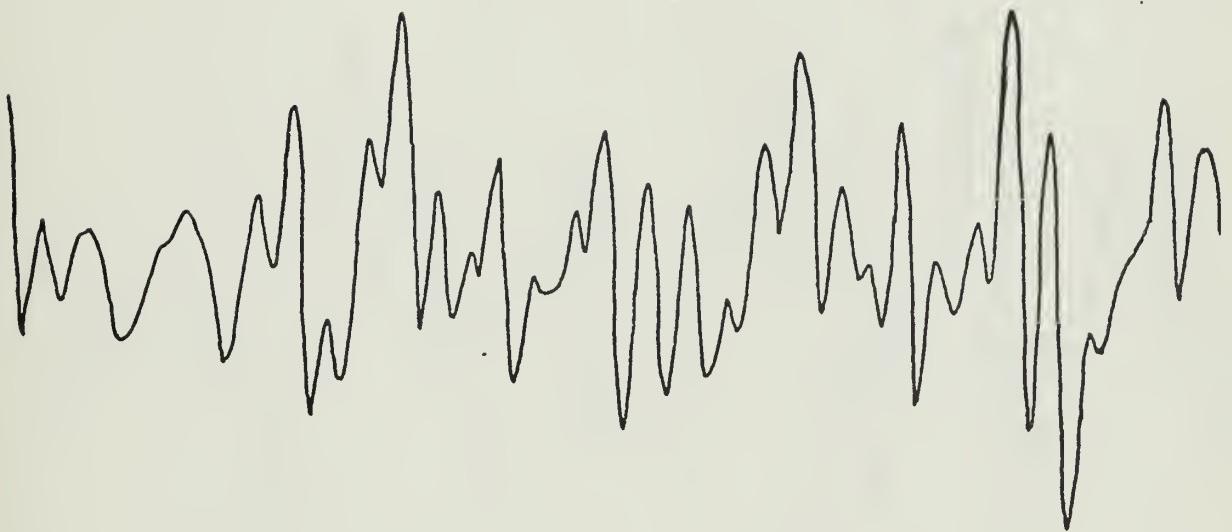


Figure 20 - 2B
(continuation)

5G

Figure 20 - 3A
(continuation)

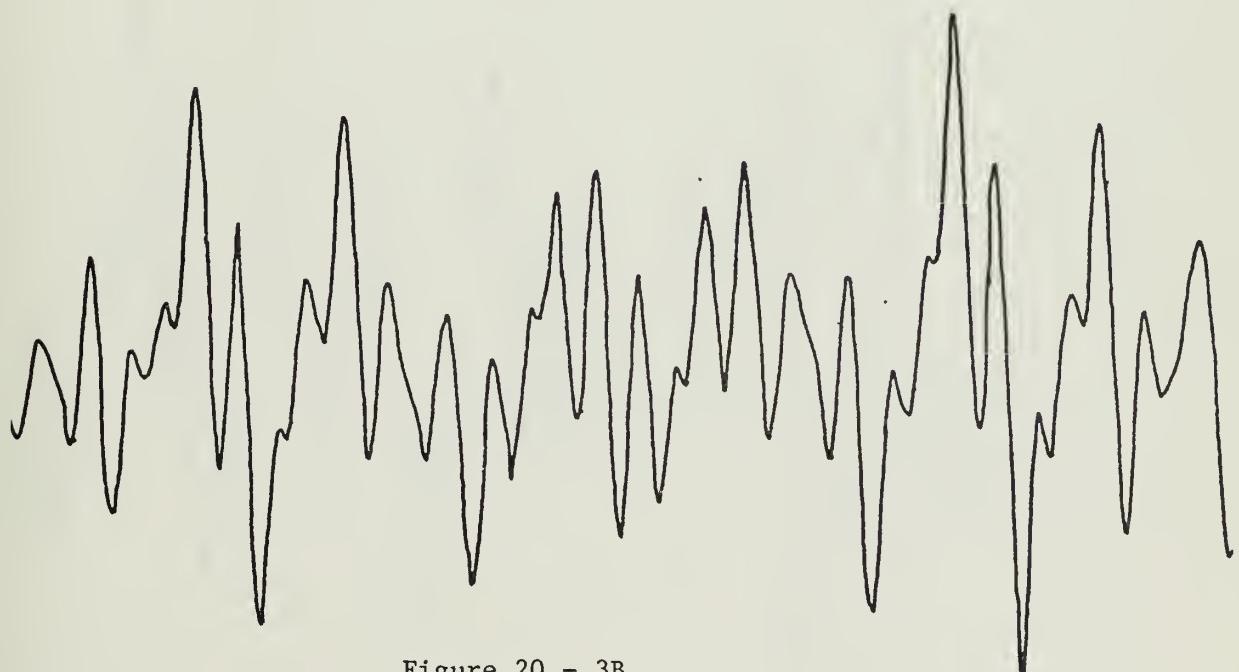
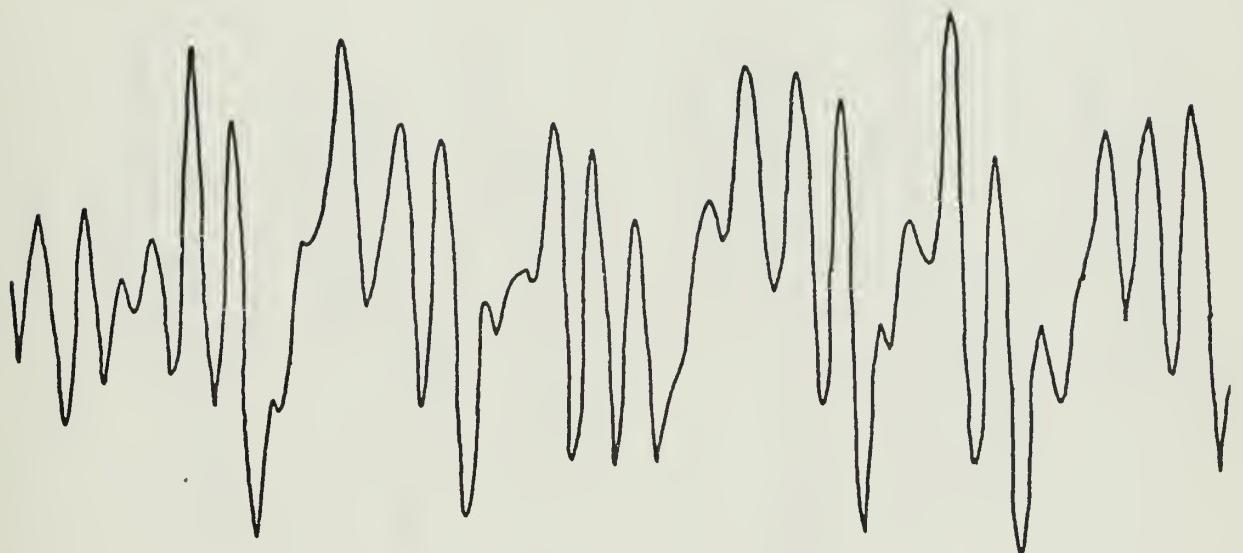


Figure 20 - 3B
(continuation)

5G

Figure 20 - 4A
(continuation)

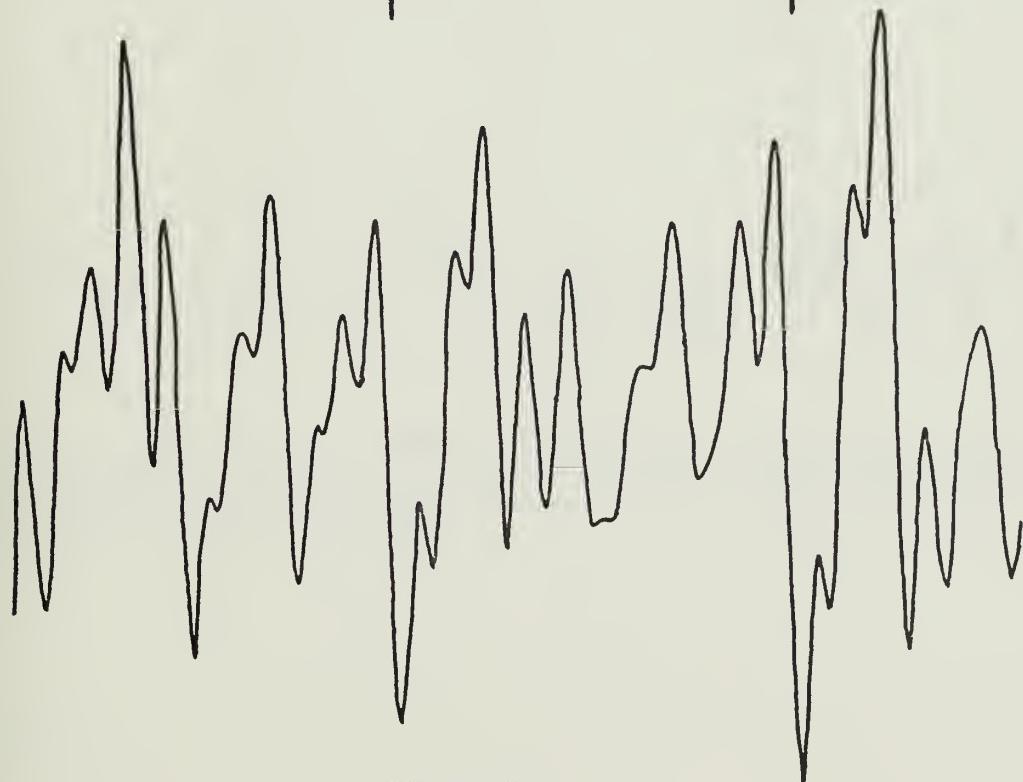
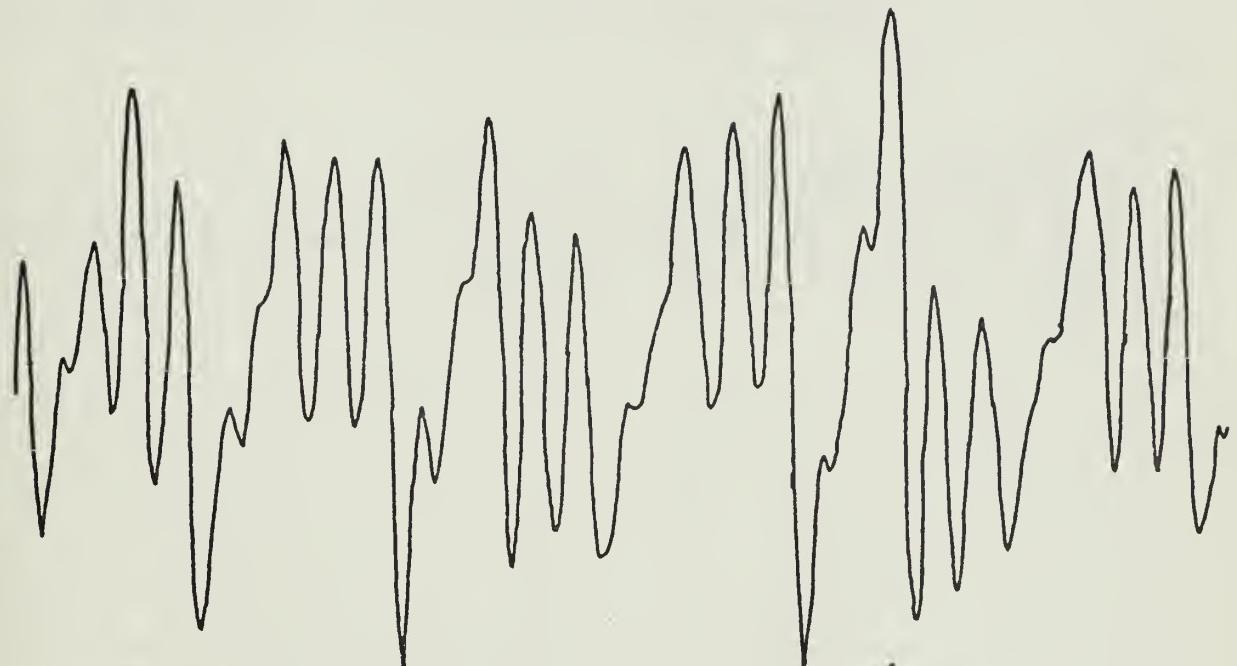


Figure 20 - 4B
(continuation)

5G

Figure 21 - 1A

Experimental ESR Spectrum of 1,5-Dimethyl-verdazyl, same Spectrum as that shown in Figure 1 but spread out on strip chart recorder

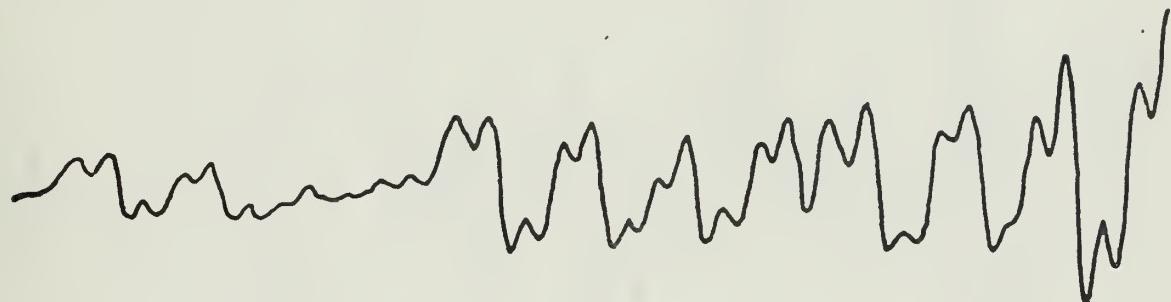


Figure 21 - 1B

Calculated ESR Spectrum of 1,5-Dimethyl-verdazyl with unsubstituted and substituted nitrogen splitting constants nearly equal (rejected as possibility, note wings above)

L
B

5G

Figure 21 - 2A
(continuation)

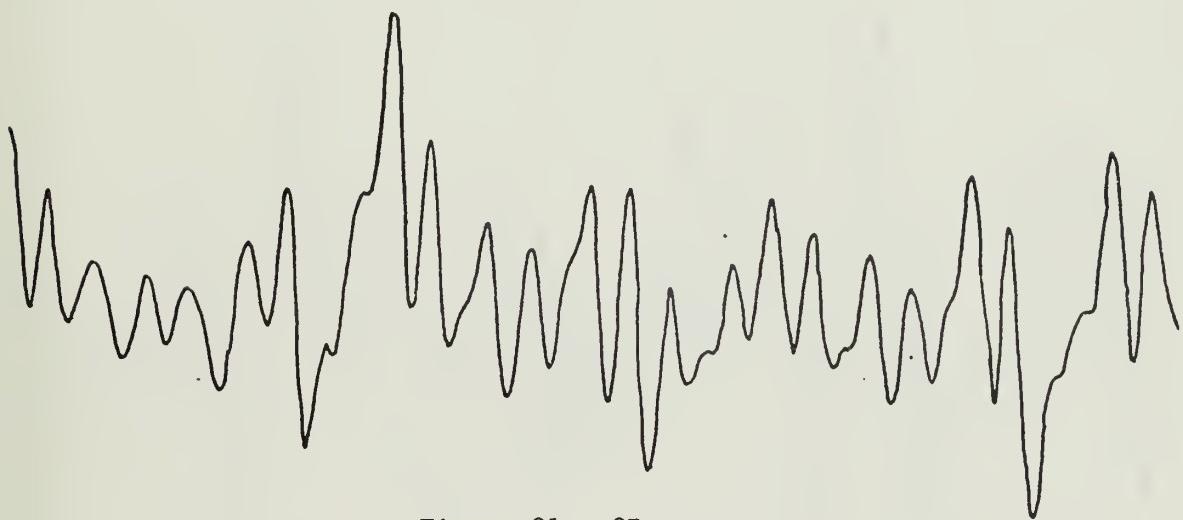
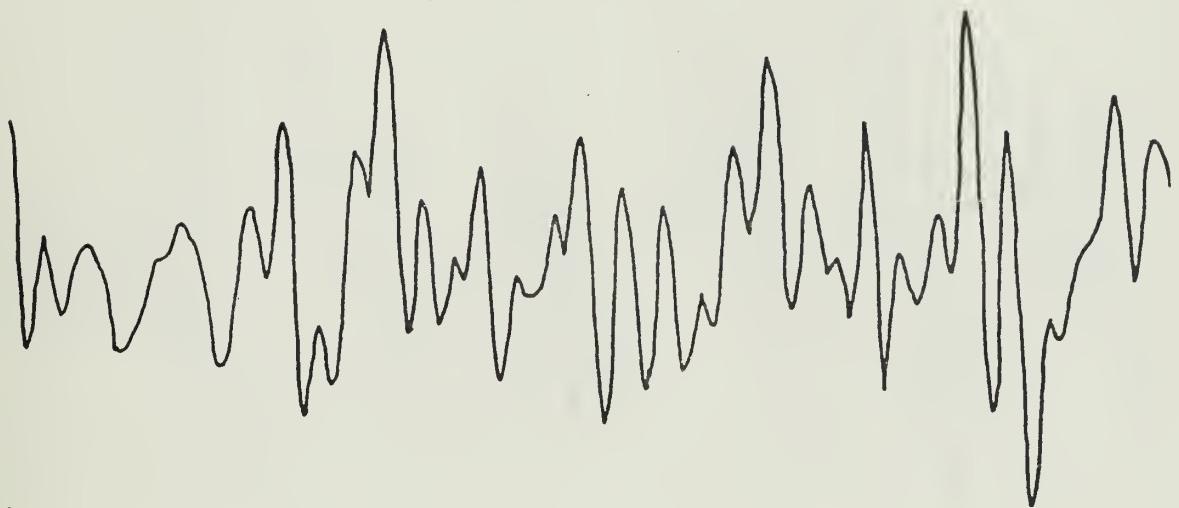


Figure 21 - 2B
(continuation)

t_{12}

5G

Figure 21 - 3A
(continuation)

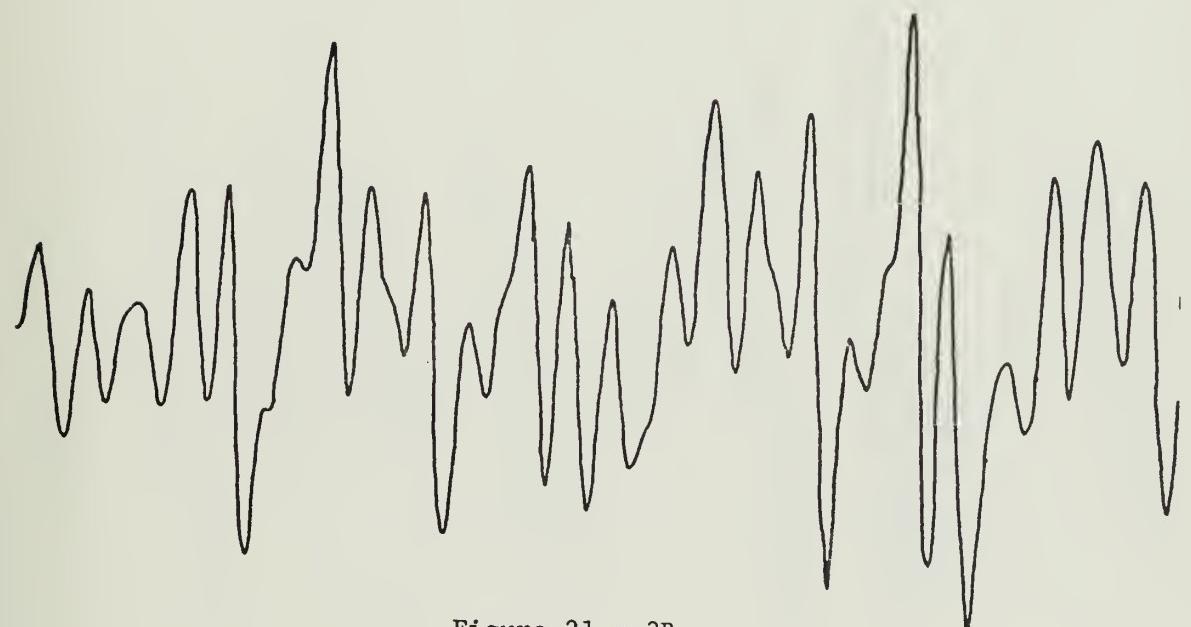


Figure 21 - 3B
(continuation)

L B

5G

Figure 21 - 4A
(continuation)

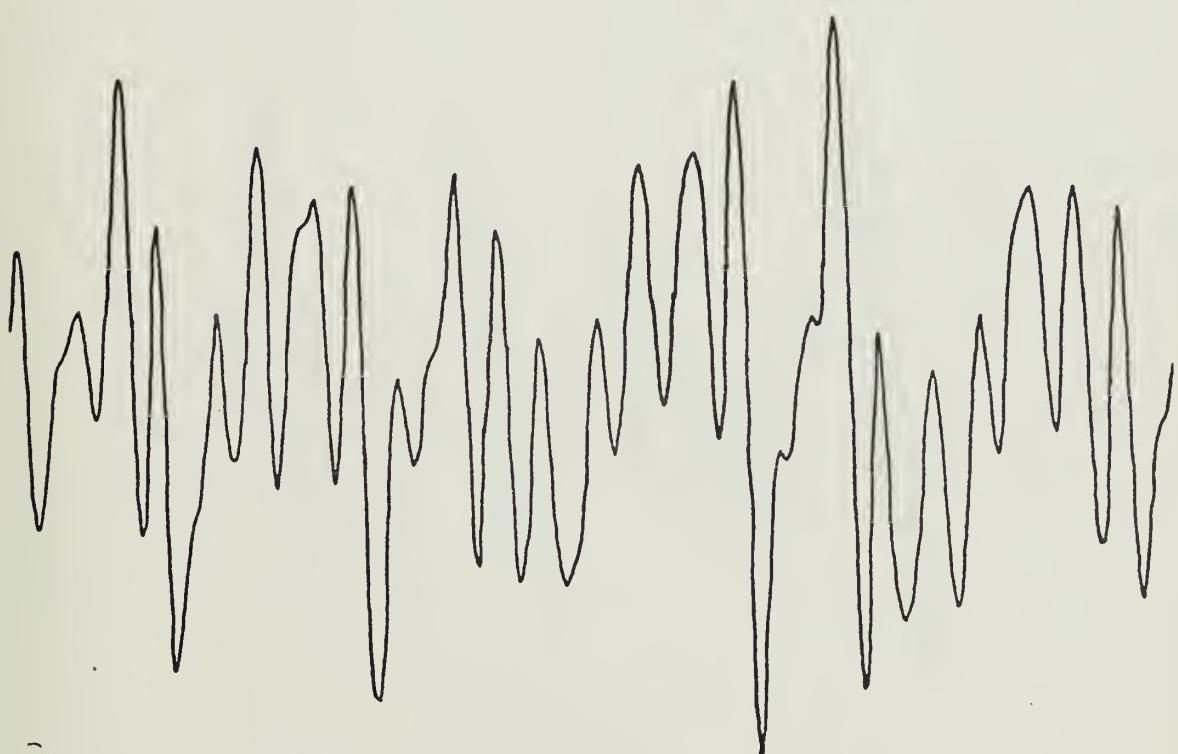
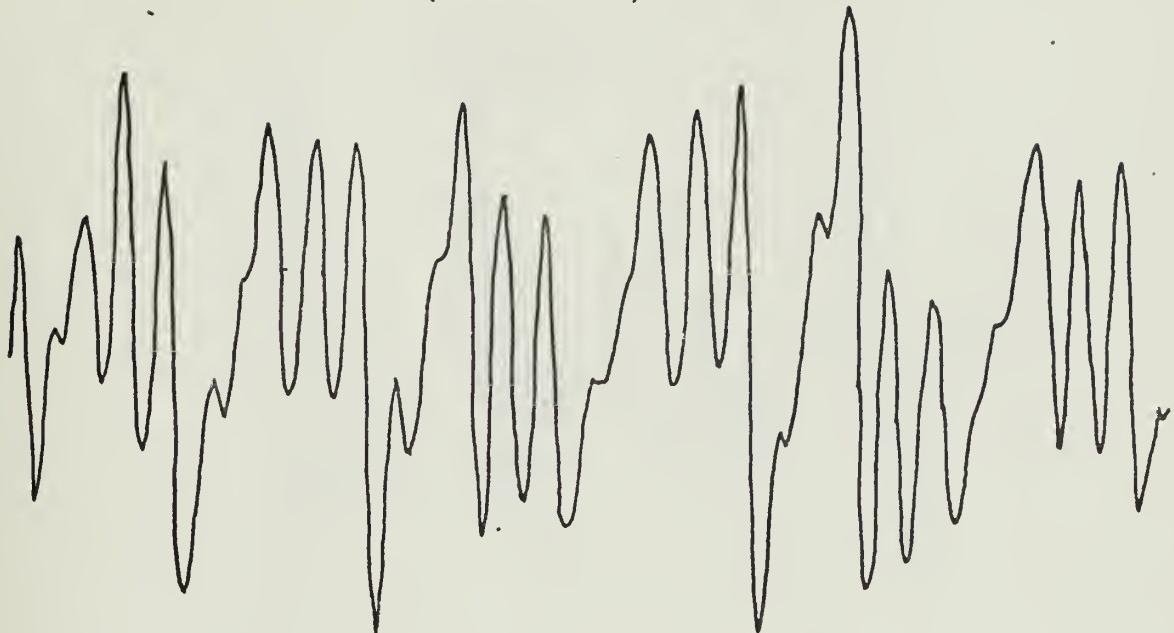


Figure 21 - 4B
(continuation)

5G



Figure 21 - 5A
(continuation)

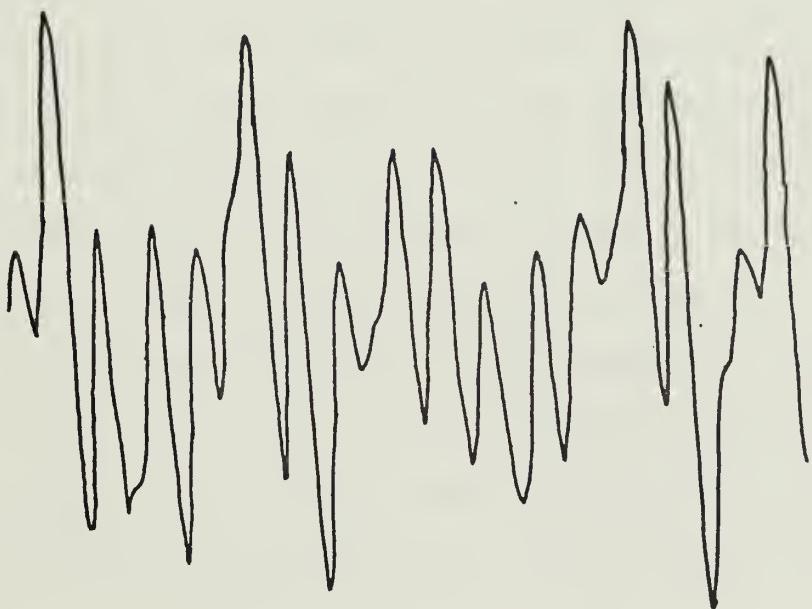
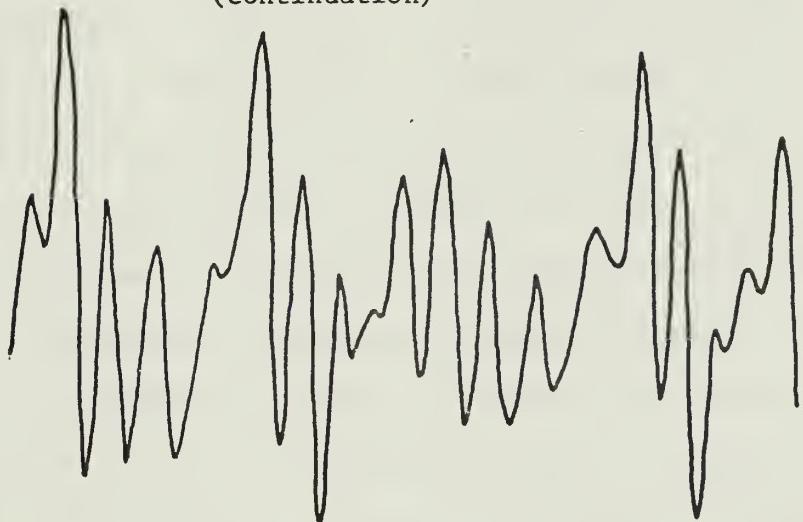


Figure 21 - 5B
(continuation)

L_B

5G

After studying the published spectra by some of these authors, it was concluded that the spectra, Figures 1 through 4, are much better resolved. Fischer²³ states that the reason bi- and triradicals are less well resolved than the monoradicals, specifically 1,5-diphenyl-verdazyl or 1,3,5-triphenyl-verdazyl is the electron-electron interaction. He goes on to say that in the ESR spectra of the biradicals, a hyperfine interaction with four nearly equivalent nitrogen atoms seems indicated, although because of the poorer resolution the observation should be interpreted cautiously. The spectra included in this project have excellent resolution, much better than any published verdazyl in the papers available; because the verdazyls considered are in a class sense different (aliphatic vs. aromatic), one cannot say absolutely that one is better resolved than the other. Possibly, aromatic substituted species will never be as well resolved as the aliphatic species because of their marked different electronic nature.

The experimentally assigned coupling constant ($a_{N_1} = 5.96$) is consistent with that calculated and those published in the literature. The coupling constant a_{N_2} is consistent with the calculated coupling constant but not with any literature values. The greatest difference in the nitrogen coupling constants published is approximately one (1) gauss.

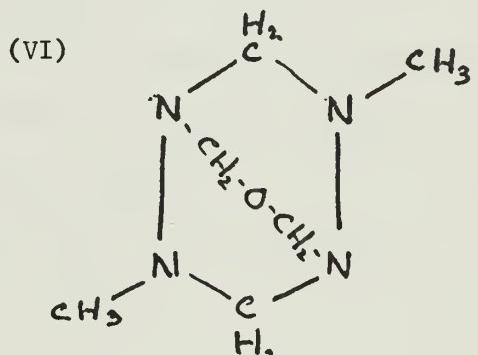
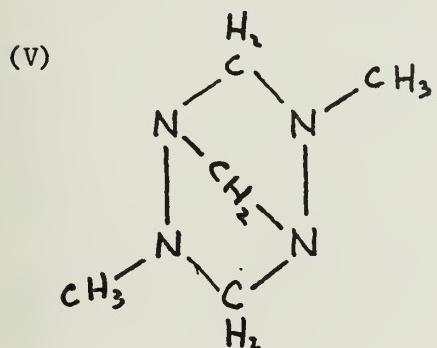
If instead of spectrum 19, spectrum 21 was chosen, the nitrogen coupling constants would be more in line with those previously reported ($a_{N_1} = 5.96$, $a_{N_2} = 3.9$); this would mean however greater electron interaction with the methyl groups outside the ring $\pi\pi$ system than with the nitrogens in the ring.

The molecular orbital parameters used in this study (Table 2) were applied to a 1,5-diphenyl-verdazyl in an attempt to compare theoretical coupling constants with those obtained by Fischer²³. His theoretical

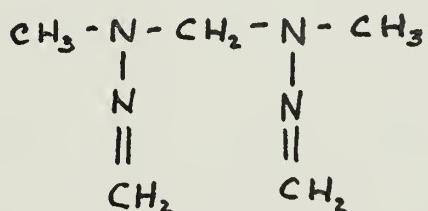
results predicted values of $a_{N_1} = 4.22$ and $a_{N_2} = 3.67$, while he observed four equivalent nitrogens with a coupling constant of 6.0 G. The values obtained in this study for 1,5-diphenyl-verdazyl were $a_{N_1} = 2.95$ and $a_{N_2} = 7.21$.

C. OTHER POSSIBLE RADICAL PRECURSOR STRUCTURES

Literature investigation and mass spectrographic analysis of pure and impure 1,4-dimethylhexahydro-s-tetrazine suggest other possible condensation products. Possibly, one of these may be the radical precursor:

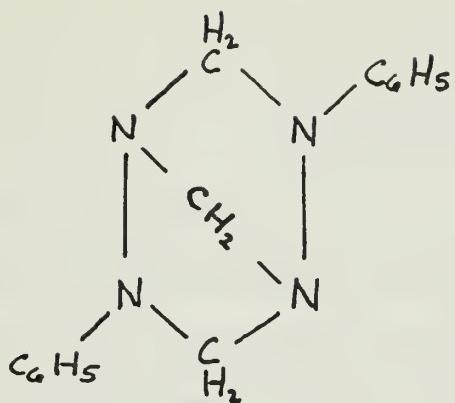


(VII)



Structure (VI) and (VII) are theorized by Schmitz and Ohme¹³ because of experimental IR -CH and -CH₂ absorption of condensation products of formaldehyde and methyhydrazine. Structure V is theorized in view of aromatic homologue VIII and mass spectrographic m/e peak 128 obtained in this project when pure and impure 1,4-dimethylhexahydro-s-tetrazine were analyzed and compared. The impure species only showed a peak at 128.

(VIII)



Each species, (V-VII), can be readily eliminated from consideration as a radical precursor because the attempts to match generated ESR spectra with the experimental spectrum failed. In addition, there was no satisfactory result in which four equivalent hydrogens existed.

There is an excellent possibility that one or all of the three are minor products but they are not the precursor in question.

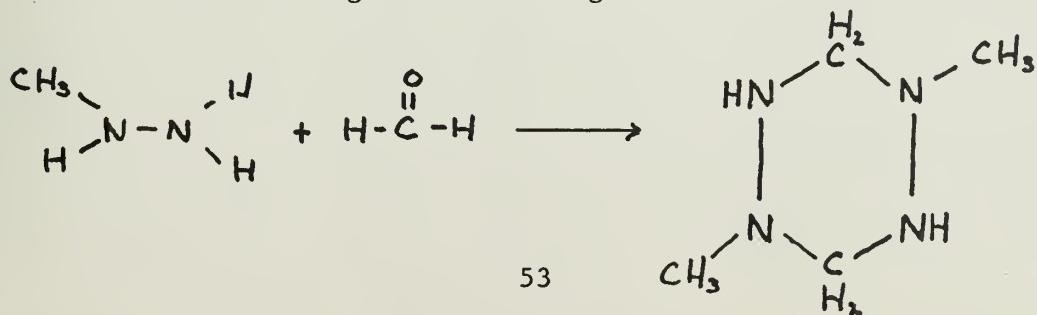
V. CONCLUSION

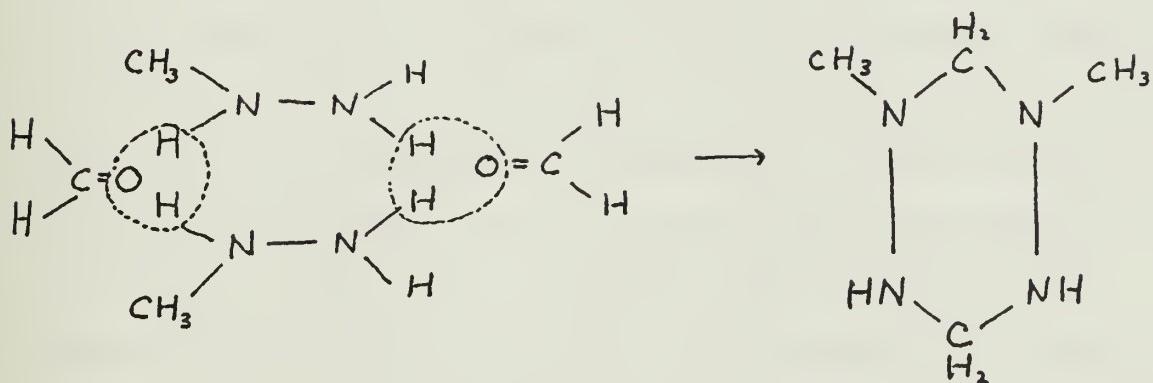
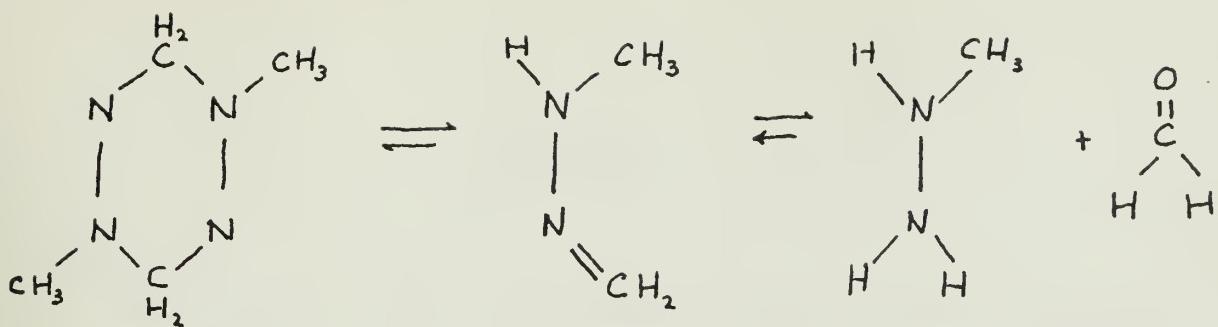
A. SUMMARY AND MECHANISM

Experimental data indicates that the radical precursor formed as a side product when formaldehyde and methylhydrazine react to form 1,4-dimethylhexahydro-s-tetrazine is 1,5-dimethyl-hexahydro-s-tetrazine and the resultant radical in solution is 1,5-dimethyl-verdazyl.

The coupling constants assigned are consistent with simple MO calculations but not with literature values developed from work on aromatic verdazyls. The literature claims the four nitrogens have almost equal electron spin densities, but some authors admit this is not absolute because of poor resolution. In this project, spectra used for study were well resolved and assignment indicates the substituted nitrogens have spin densities just about half those of the non-substituted nitrogens. If a poorly fitting spectrum was accepted, the nitrogen coupling constants would agree with previous researchers conclusions.

This paper reports the first aliphatic verdazyl, and because of the different electron environment in aliphatic and aromatic substituted six membered heterocyclics, there is reason to believe the conclusions reached on spin densities are correct. In addition considering the chemistry already known about hydrazones (hydrazones hydrolyze to give the original aldehyde/ketone and hydrazine) the radical precursor postulated is quite feasible formed through the following mechanism:





B. RECOMMENDATIONS FOR FURTHER INVESTIGATION

Additional work should be performed to prove absolutely the thesis presented, and in this light the following is recommended:

- (1) Extended chromatographic work.
- (2) A more sophisticated MO calculation.
- (3) Preparation and analysis of homologues of this system.
- (4) Extended NMR studies emphasizing longer periods of time at each temperature, and low temperature work.
- (5) UV/VIS spectral characterization of the verdazyl.

Appendix A

Program Use.

The program is ready for use when two text lines with a blinking cursor appear in the upper right hand corner of the 14x14 display screen. To enter a spectrum for calculation and display, the operator types a 1. at the ready position and advances the cursor automatically to the next correct position by depressing the return key. Once the parameters described in the documented program (. follows .) have been entered the cursor automatically returns to the ready position when the return key is depressed following entry of the last desired parameter. To display the spectrum once again the return key is depressed, after a maximum of 20 seconds the blinking cursor reappears on the screen. To enter a new spectrum proceed as previously described. To change any parameter type its location (line 2 item 3 would require 23.), make the correction and proceed as before. Figure 22 depicts the video display in various sequential phases. To integrate a spectrum simply proceed as described above using a MODCUR value of 1.; a MODCUR value of 2. will store the plot on the screen as a dashed line display; a MODCUR value of 3. will erase any dashed line plot.

Calibration of the video display is accomplished by plotting a known simple ESR spectrum with a splitting constant of an inch or more and measuring the ordinate and abscissa displayed on the screen with a simple measuring device. A two hydrogen spectrum is recommended with a split of 2 inches and a vertical intensity of 3 inches. A plastic overlay representing an experimental spectrum is most helpful in assignment work.

Text Display Ready for Parameter input:

NOSETS	MORE	MODCUR	NUMPTS	PTOP	FINT	FLDMIN	FLDMAX	SCALE	
CASE	SPLT	CASE	SPLT	CASE	SPLT	CASE	SPLT	CASE	SPLT

"The cursor in the upper right hand corner will be blinking."

Text Display Ready for Execution:

NOSETS	2.	MORE	0.	MODCUR	0.	NUMPTS	900.	PTOP	.2	FINT	2.	FLDMIN	-7.	FLDAX	7.	Scale	1.
CASE	1.	SPLT	2.22	CASE	7.	SPLT	5.33										

"Now hit the return key and in approximately 20 seconds the display will appear on the screen."

Making a change to the above set of parameters, splt one for example:

NOSETS	2.	MORE	0.	MODCUR	0.	NUMPTS	900.	PTOP	.2	FINT	2.	FLDMIN	-7.	FLDAX	7.	SCALE	1.
CASE	1.	SPLT	1.98	CASE	7.	SPLT	5.33										

"Hit the return key and the cursor will start blinking, hit it again and the display will appear."

Figure 22:

Appendix B

Some Operational Procedures and Recommendations IN USE of the XDS 9300 and ADAGE AGT10

The computer system as installed at the NPS Electrical Engineering Laboratory is a "hands on" operation. The user operates the complete system independently. The following operational techniques have been developed.

1. Prior to loading any graphics program into the system, clear memory by depressing "CLEAR" and "CLEAR FLAGS" on the XDS 9300 control panel simultaneously. This procedure precludes picking up any extraneous information from memory because of an earlier user's program.
2. If the graphics display is stopped for an unknown reason or mistake, the following procedure should be followed to return to an operational mode: Clear the instruction register on the XDS 9300 with the computer in idle, enter 401(N) (where N is five octal digits) in the instruction register (N is obtained from the computer location map and is found immediately following 9INITIAL). Then depress "STEP" and "RUN" sequentially. If the outlined procedure fails, the program must be re-loaded from cards or magnetic tape.
3. If a feed check occurs during a card loading operation, it can be corrected by following the procedure in the operator's manual with one exception; if the feed check occurs during a data reading sequence, the program must be reloaded.
4. The installed card reader's performance can be improved if a slight finger pressure is applied to the card weight during the card reading procedure.

Operating procedures are well documented in the OPERATOR'S MANAUL FOR
THE GRAPHICS DISPLAY SUBSYSTEM distributed to users by the Department of
Electrical Engineering Computer Laboratory.

Appendix C
 Impact Test Data on 1,4-Dimethyl-hexahydro-s-tetrazine
 (material was very impure, a yellow color)

$$RSP = 1.0 - \frac{(N-2)}{(T-1.0)}$$

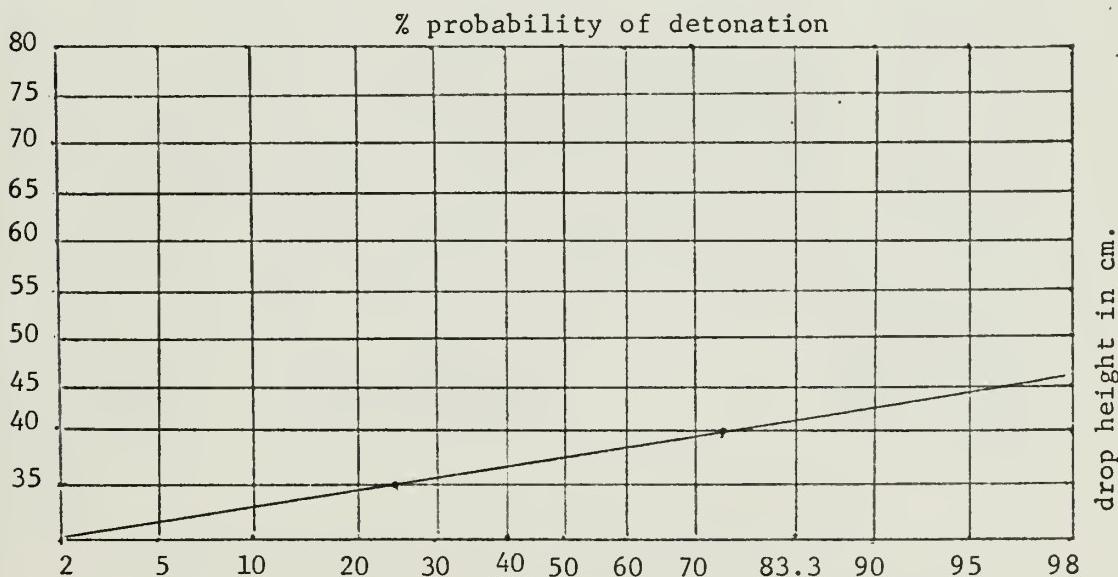
N = no. of 5cm. increments

T = no. of recorded tests

RSP = 50.0

FPP = 38 cm

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	%
95	E	e	e	e	e	e	e	e	e	e					e	e	e	e	e	e	e	e	e	e	100.0	
90		E	e	e	e	e	e	e	e	e					e	e	e	e	e	e	e	e	e	e	100.0	
85			E	e	e	e	e	e	e	e					e	e	e	e	e	e	e	e	e	e	100.0	
80				E	e	e	e	e	e	e					e	e	e	e	e	e	e	e	e	e	100.0	
75					E	e	e	e	e	e					e	e	e	e	e	e	e	e	e	e	100.0	
70						E	e	e	e	e					e	e	e	e	e	e	e	e	e	e	100.0	
65							E	e	e	e					e	e	e	e	e	e	e	e	e	e	100.0	
60								E	e	e					e	e	e	e	e	e	e	e	e	e	100.0	
55									E	e	e				e	e	e	e	e	e	e	e	e	e	100.0	
50										E	e	e			e	e	e	e	e	e	e	e	e	e	100.0	
45											E	e	e			e	e	e	e	e	e	e	e	e	100.0	
40												E	e			N	E	E		N	E				75.0	
35													E	N	n		N		N	n					N	25.0
30														N	n	n		n	n	n	n				n	0.0




```

C FORTRAN IV PROGRAM FOR CALCULATION AND DISPLAY OF ESR
C SPECRTA
C DEVELOPED FOR XDS 9300/ADAGE AGT10
C W.M.TOLLES AND R.S.WATKINS SEPTEMBER 1970
C *** THE FOLLOWING ARE THE ONLY ARGUMENTS NEEDED
C NSETS = NUMBER OF SETS TO BE USED (1****6)
C MORE = 0 OR 1, ALLOWS SUPERPOSITION OF SPECTRA IF 1
C MODCUR =(,0,1,2,3)
C   0 = FIRST DERIVATIVE PLOT
C   1 = INTEGRATED PLOT
C   2 = STERE PL9T AS DASHED LINE
C   3=ERASE DASHED LINE PLOT
C NUMPTS = 900 NORMALLY BUT AS YOU DESIRE
C PTOP = PEAK TO PEAK LINE WIDTH AS DESIRED (IE .22)
C FINT = HEIGHT OF MOST INTENSE LINE (.1E 3.25 )
C FLDMIN = FIELD MINIMUM,LOW FIELD POSITION (IE -33.0)
C FLDMAX = FIELD MAXIMUM,HIGH FIELD POSITION (IE 7.0)
C SCALE = ALLOWS SCALING OF ABSICSA
C CASE = CASE AS SELECTED FROM DATA SET
C   .....CASE 1 = 1H
C   .....CASE 2 = 2H
C   .....CASE 3 = 3H
C   .....CASE 4 = 4H
C   .....CASE 5 = AS YOU REQUIRE, 2NH NEW
C   .....CASE 6 = 6H
C   .....CASE 7 = 1N
C   .....CASE 8 = 2N
C   .....SPLT = MEAS. SPLITTING CONSTANT
C MAIN PROGRAM
C COMMON/IMAG/IMAGE(902)
C DIMENSION IDIRG(3),IDIRT(30),IPSS(4:24),IHED(20),IDAT(
C 12,4:24),IHEE(24)
C 1,C(900),D(900),FIA(2000)
C DIMENSION SP(8,16),IN(8,16),A(2000),ICASE(12),SPLT(12)
C DATA NULL/7777777B/

```



```

DATA 1P0$/1,10,19,28,37,46,55,64,73,1,9,17,25,33,41,49
1,57,65,73,81,89/
EQUIVALENCE (FIA,D)
NAMELIST IDEV,IER
IDEV=1
OUTPUT(101)'TYPE IDEV=2 IF USING AGT2'
INPUT(101)
DGINIT••INITIALIZES AGT10 GRAPHICS DISPLAY SUBSYSTEM
C ARGUMENTS IDEV= INTEGER (1IER2)SPECIFYING AGT SUBSYSTEM
C IDIRG=FIRST WORD ADDRESS OF GRAPHIC DIRECTORY
C IERROR = ERROR FLAG
C CALL DGINIT(IDEV, IDIRG, IER)
C IF(IER.NE.0)OUTPUT(101)IER,' DGINIT ERROR'
C DGINIT••INITIALIZES AGT10 TEXT DISPLAY SUBSYSTEM
C ARGUMENTS IDEV = AS BEFORE
C IDIR = ADDRESS OF TEXT DIRECTORY BUFFER
C NDIR=INTEGER NUMBER OF WORDS IN TEXT DIRECTORY
C IERROR = ERROR FLAG
C CALL DTINIT(IDEV, IDIRT, 30,IER)
C IF(IER.NE.0) OUTPUT(101)IER,' DGINIT ERROR'
C ENCODE(81,500,IHED)
500 FORMAT(1NESETS MORE M0DCUR NUMPTS PTSP F
CINT FLDMAX SCALE ')
C TEXTS•• CALLED TO OUTPUT A FULL LINE OF TEXT IN AGT10
C ARGUMENTS IDEV = AS BEFORE
C ITEXT = ADDRESS OF BCD ARRAY TO BE OUTPUT
C NWORD= NUMBER OF WORDS IN TEXT ARRAY TO BE
C OUTPUT
C LN = LINE NUMBER FOR DISPLAY
C ICP0S = STARTING CHARACTER POSITION
C ISIZE = CHARACTER SIZE (INTEGER 1,2 OR 3)
C INT = INTENSITY (INTEGER 1,2 OR 3)
C IERROR = AS BEFORE
C CALL TEXT(IDEV,IHED,20,1,1,3,IER)
C IF(IER.NE.0)OUTPUT(101)IER,' TEXTS ERROR'

```



```

ENCODE(96,550,IHEE)
550 FORMAT('CASE SPLT CASE SPLT CASE SPLT CASE SPLT')
1 CASE SPLT CASE SPLT CASE SPLT CASE SPLT
CALLTEXTS(IDEV,IHEE,24,4,1,3,IER)
IF(IER.NE.0)OUTPUT(101)IER,1 TEXT8 ERROR!
D0 2 I = 1,8
  READ(5,1000) (SP(I,J), J = 1,16)
2 READ(5,1001) (IN(I,J), J = 1,16)
D0 16 I = 1,8
  IQ = IN(I,1)
  WRITE(6,1022) (I)
  WRITE(6,1010) (SP(I,J), J = 2,IQ)
16  WRITE(6,1011) (IN(I,J), J = 2,IQ)
  D0 501 I=4,24
  D0 501 J=1,2
501 IDAT(J,I)=NULL
  3 CONTINUE
1   CONTINUE
      LDA      =06011022
      STA      065551
C   TEXT8•OUTPUTS A TEXTBLOCK TO AGT10 WITH BLOCK
C   AUTOMATICALLY SELECTED FOR EDITING AT AGT
C   FOR EDITING AT THE AGT
C   ARGUMENTS SAME AS FOR TEXT8
6   CALL TEXT8(IDEV,NULL,1,1,90,1,3,IER)
    IF(IER.NE.0)OUTPUT(101)IER,1 NULL NC!
7   IF(MOD(IDIRT(3),8).EQ.0) G9 T9 7
C   TEXT1•••INPUTS UP TO A FULL LINE OF TEXT FROM AN AGT10
C   ARGUMENTS IDEV = AS BEFORE
C   ITEXT=ADDRESSES OF ARRAY WHERE BCD IS TO BE PLACED
C   NWORD = NUMBER OF WORDS IN ITEXT ARRAY ARE TOBE RCVD.
C   (INTEGER 1•••••24 )
C   LN = LINE NUMBER (1••••40 )
C   ICPOS = CHARACTER POSITION OF BLOCK NUMBER
C   IERR8 = AS BEFORE

```



```

CALL TEXTI(IDEV,NC,1,0,3,IER)
IF(IER•NE.0) OUTPUT(101) IER, ! NC'
DECODE(4,506,NC) NC
FORMAT(14)
506 IF(NC•EQ.0) GO TO 555
IF(NC•GT.20•AND•NC•LT.27) N1=N2=11+2*(NC-20),GOT0601
IF(NC•GT.10•AND•NC•LT.20) M1=M2=NC-7; GO TO 11
IF(NC•NE.1) GO TO 6
M1=4; M2=12; N1=13

11 CONTINUE
DO 502 I = M1,M2
CALL TEXTR(IDEV, IDAT(1,1), 2, 2, IPSS(I), 1, 3, IER)
IF(IER•NE.0)OUTPUT(101)IER, !
503 IF(M9D(IDIRT(I),8)•EQ.0)GOT0503
CALL TEXTI(IDEV, IDAT(1,1), 2, 0, I, IER)
IF(IER•NE.0)OUTPUT(101)IER, !
502 CONTINUE
DECODE(72,504, IDAT)NESETS, MORE, M9DCUR, NMPTSS, PTOP, FINT
1FLDMIN,FLDMAX,SCALE
504 FORMAT(418,5F8.4)
IF(M9DCUR.LE.1) GO TO 660
IF(M9DCUR.NE.2)GOT0650
WRITE(6,577) M9DCUR,NC
577 FORMAT(' PASS THROUGH STORAGE OF BLOCK 1 INTO 2 WITH M
10DCUR AND NC EQUAL T8',215)
IMAGE(1)=IHEAD(1,2)
LDA      =06011005
STA      06551
CALL GRAPH0(IDEV, IMAGE, NMPT2, 2, IER)
IF(IER•NE.0)OUTPUT(101)IER, !
GRAPH0 ERROR!
GO TO 1
650 IF(M9DCUR.NE.3)GOT0660
IMAGE(1)=IHEAD(0,0)
LDA      =06011005
STA      06551

```



```

CALL GRAPH8(IDEV, IMAGE, NMPT2, 2, IER)
IF(IER•NE•0)GOUTPUT(101)IER, ! GRAPHS ERROR!
GO TO 1
IF(NC•NE•1) GO TO 1
N2=11+2*NSETS
CONTINUE
660
S      LDA      -06011022
S      STA      06551
D0 551 I=N1,N2,2
CALL TEXTR(IDEV, IDAT(1,1), 2, 5, IPOS(I), 1, 3, IER)
IF(IER•NE•0)GOUTPUT(101)IER, ! TEXT8 ERROR!
552 IF(MOD(IDIRT(I), 8)•EQ•0) GOTO 552
CALL TEXTI(IDEV, IDAT(1,1), 2, 0, I, IER)
IF(IER•NE•0)GOUTPUT(101)IER, ! TEXT8 ERROR!
CALL TEXTR(IDEV, IDAT(1,1+1), 2, 5, IPOS(I+1), 1, 3, IER)
IF(IER•NE•0)GOUTPUT(101)IER, ! TEXT8 ERROR!
553 IF(MOD(IDIRT(I+1), 8)•EQ•0) GOTO 553
CALL TEXTI(IDEV, IDAT(1,1+1), 2, 0, I+1, IER)
IF(IER•NE•0)GOUTPUT(101)IER, ! TEXT8 ERROR!
551 CONTINUE
GO TO 6
555 DECODE(16*NSETS, 554, IDAT(1,13))((ICASE(I), SPLT(I)), I=
11, NSETS)
554 FORMAT(6(18,F8.4))
IF(NSETS) 12, 2000, 12
12 CONTINUE
DIFF = FLDMAX•FLDMIN
FNUM1 = NUMPTS-1
FINCR = DIFF/FNUM1
WRITE(6,1021)
WRITE(6,1012) NSETS, MORE, MDCUR, NUMPTS, PT9P, FININT, FLDIM
1 IN, FLDMAX
NMPT2 = NUMPTS+2
IF(MORE•EQ•0) TINT = FININT
IF(MORE•NE•0) GO TO 204

```



```

D8 4 I = 1,900
4 C(1) = 0.0
204 CONTINUE
    DUM1=0.0
    WRITE(6,1013) ((ICASE(I), SPLT(I)), I = 1,NSETS)
C SUBROUTINE CALSPL = CALCULATES POSITION AND INTENSITY OF
C EACH LINE
C CALL CALCSPL(NSETS, ICASE, IN,A,FIA,SP,SPLT,IX)
C IF THE TOTAL NUMBER OF LINES CALCULATED EXCEEDS 2000 THE
C ERROR MESSAGE •••THE ARRAY DIMENSION HAS BEEN EXCEEDED WITH
C XXXX LINES••• IS PRINTED
    IF(IX.LE.2000) GO TO 83
    WRITE(6,1030) IX
1030 FORMAT(//,' THE ARRAY DIMENSION HAS BEEN EXCEEDED WITH
1,'15,', 'LINES', //++)
    GO TO 6
83 D8 84 I = 1,IX
84 A(I) = A(I) + DUM1
    FIAMAX = 0.0
    FSUM = 0.0
    D8 1082 I = 1,IX
    FSUM = FSUM+FIA(I)
    IF(FIA(I)-FIAMAX) 1082,1082,1081
1081 FIAMAX = FIA(I)
    1082 CONTINUE
    FVAR = FINIT*100.0/(FSUM*PT9P**2)
    D8 1083 I = 1,IX
1083 FIA(I) = FIA(I)*FVAR
    IF(MORE.EQ.0) GO TO 1085
    D8 1084 I = 1,NUMPTS
1084 C(I) = C(I)/DDCMX
    1085 CONTINUE
    C SUBROUTINE CURVE = PLOTS THE CALCULATED CURVE
    200 CONTINUE
    CALL CURVE(IX,PT9P,FLDMIN,FLDMAX,FINCR,NUMPTS,A,FIA,C,

```



```

1CMAX,MODCUR)
122 DDCMX = ABS(TINT)/(CMAX*5.0)
D8 125 I = 1,NUMPTS
125 C(I) = C(I)*DDCMX
OFFSET=0.0
      IF(MODCUR.EQ.1) OFFSET=-0.75
128 D8 129 I = 1,NUMPTS
129 C(I) = C(I)+OFFSET
FLD = (FLDMIN-FLDMAX)/2.0
IF(SCALE.EQ.0.0) SCALE = 1.0
D8 5 I = 1,NUMPTS
D(I) = SCALE*FLD/5.0
5 FLD = FLD+FINCR
      IHEDD...CONSTRUCTS THE ONE WORD HEADER OF A GRAPHIC
C DATA BLOCK TO BE DISPLAYED BY SUBSEQUENT INVOCATION
C OF GRAPHIC OR GRAPHR
C ARGUMENTS IDISH = 0,1 SOLID LINES /DASHED LINES
C INT = DISPLAY INTENSITY (0....10 )
C IMAGE(1)=IHEAD(0,10)
C IPACK...PACKS THE X AND Y AND THE MOVE DRAW INDICATOR
C OF THE COORDINATE POINT INTO ONE WORD OF A GRAPHICS
C DATA BLOCK WHICH IS TO BE TRANSMITTED TO AN AST10
C BY INVOKING GRAPHIC OR GRAPHR
IMAGE(2) = IPACK(D,C,O)
DA 505 I=3,NMPT2
J=I-2
505 IMAGE(I)=IPACK(D(J),C(J),1)
LDA      06011005
S STA      06551
S CALL GRAPHIC(IDEV,IMAGE,NMPT2,IER)
IF(IER.NE.0)OUTPUT(101)IER,1,GRAPH ERROR!
135 GO T9 3
2000 STOP
1000 FORMAT (16F5.0)
1001 FORMAT (16I5)

```



```

1002 FORMAT (4I5, 8F5.4, 2E8.1, 2I2)
1003 FORMAT (8(15,F5.3))
1004 FORMAT (6A8)
1009 FORMAT (1H1)
1010 FORMAT (1H ,8F10.5)
1011 FORMAT (1H ,8(6X,14))
1012 FORMAT (4I8,8F10.5)
1013 FORMAT (1H ,8(12,F8.4,2X))
1014 FORMAT (//)
1015 FORMAT (1H ,15F6.2)
1016 FORMAT (1H ,15I6)
1017 FORMAT (1H ,15F6.3)
1020 FORMAT (//)
1021 FORMAT (71H NSETS MORE M3DCURV NUMPTS PT9P
1          1 FINT FLDMIN FLDMAX )
1022 FORMAT (5H CASE, 12)
1023 FORMAT (39H GRAPH NOT PLOTTED DUE TO ERROR IN DATA)
END

```

C


```

SUBROUTINE CURVE(IX,PTOP,FLDMIN,FLDMAX,FINCR,NUMPTS,A,
1FIA,C,CMAX,MDCUR)
DIMENSION A(1),FIA(1),C(1)
W = PTOPI*0.8660254
WS = W*W
FLD = FLDMIN+FINCR
CMAX = 0.0
PTOPY = 8.0*PTOP
IMIN = 1
IMAX = 1
D0 120 I = 1,NUMPTS
FLD = FLD+FINCR
FMIN = FLD-PTOPM
FMAX = FLD+PTOPM
87 IF(A(IMIN)-FMIN) 88,91,91
88 IF(IMIN-IX) 89,91,91
89 IMIN = IMIN+1
G0 T0 87
91 IF(A(IMAX)-FMAX) 92,95,95
92 IF(IMAX-IX) 93,95,95
93 IMAX = IMAX+1
G0 T0 91
95 IF(MDCUR.NE.0) G0 T0 195
D0 110 J = IMIN,IMAX
AJ = A(J)-FLD
DENOM = WS + AJ*AJ
110 C(I) = C(I) + (FIA(J)*WS*AJ)/(DENOM*DENOM)
IF(ABS(C(I))-CMAX).120,120,118
118 CMAX = ABS(C(I))
G0 T0 120
195 D0 210 J = IMIN,IMAX
210 C(I) = C(I) + FIA(J)/(WS+(A(J)-FLD)*2)
IF(ABS(C(I))-GT.CMAX) CMAX=ABS(C(I))
120 CONTINUE
RETURN

```



```

SUBROUTINE CALCSP(NSETS,ICASE,IN,A,FIA,SP,SPLT,N0)
DIMENSION ICASE(12), IN(8,16), A(1), FIA(1), SP(8,16),
1SPLT(12)

A(1) = 0.0
FIA(1) = 1.0
N0 = 1
N0J = 1
N0K = 2
D0 50 I = 1,NSETS
IC = ICASE(I)
IQ = IN(IC,1)
IF (N0 .GT. 2000) RETURN
N0 = N0*(IQ-1)
N0I = N0+1
D0 30 J = 1,N0J
N0K = N0K-1
D0 20 K = 2,IQ
N0I = N0I-1
IQ2K = IQ2-K
A(N0I) = A(N0K)+SP(IC,IQ2K)*SPLT(I)
20 FIA(N0I) = FIA(N0K)*IN(IC,IQ2K)
30 CONTINUE
CALL SHLSRT(A,FIA,N0)
NN = 1
ICL = 1
ICU = 2
52 IF(ICL.GT.N0) G0 T0 59
      IF(ICU.GT.N0) G0 T0 58
      IF(ABS(A(ICU)-A(ICL)).GT.1.0D-06) G0 T9 58
53 ICU = ICU+1
      IF(ICU.GT.N0) G0 T0 54
      IF(ABS(A(ICU)-A(ICL)).GT.1.0D-06) G0 T9 54
      G0 T0 53
54 ICU = ICU-1

```



```

FF = 0.0
D0 55 II = ICL,ICU
55 FF = FF+FIA(II)
FFS = FF
FF = 0.0
D0 56 II = ICL,ICU
56 FF = FF+FIA(II)*A(II)
A(NN) = FF/FFS
FIA(NN) = FFS
ICL = ICU+1
ICL = ICL+1
ICU = NN+1
NN = NN+1
G0 T0 52
58 FIA(NN) = FIA(ICL)
A(NN) = A(ICL)
ICL = ICU
ICU = ICL+1
NN = NN+1
G0 T0 52
59 NB = NN-1
NBK = NB+1
NBJ = NB
50 CONTINUE
FMAX = 0.0
D0 60 I = 1,NB
IF(FIA(I).LE.*FMAX) G0 T0 60
FMAX = FIA(I)
60 CONTINUE
D0 65 I = 1,NB
65 FIA(I) = FIA(I)/FMAX
RETURN
END

```


SUBROUTINE SHLSRT (A,FIA,N)

DIMENSION A(1),FIA(1)

M1 = 1

6 M1 = M1*2

IF (M1=N) 6,6,8
8 M1 = M1/2-1

MM=M1

20 MM= MM/2
IF (MM) 99,100,21

21 K = N-MM

IF (K) 99,99,22

22 DO 1 J=1,K
1 I=J

11 IM=I+MM
IF (A(IM)=A(I)) 30,1,1

30 TEMP = A(I)
ITEMP = FIA(I)

A(I)=A(IM)
FIA(I)=FIA(IM)

A(IM)=TEMP
FIA(IM)=ITEMP

I1 = I1-MM
IF (I1) 1,1,11

1 CONTINUE

100 GO TO 20

100 RETURN
99 WRITE(6,999) MM,K,I1,J
999 FORMAT(20H PROGRAM ERROR
END

-0.5 0.5
3 1 1
4 -1.0 0.0 1.0
4 1 2 1

	-1.5	0.5	1.5
5	-1	3	1
	-2.0	-1.0	0.0
6	-1	4	6
	-3.0	-2.0	-1.0
8	-1	6	15
	-3.0	-2.0	-1.0
8	-1	6	15
	-1.0	0.0	1.0
4	-1	1	1
	-2.0	-1.0	0.0
6	1	2	

	0.5	2.0
5	3	1
	0.0	1.0
6	4	1
	0.0	1.0
8	20	15
	0.0	1.0
8	20	15
	1.0	2.0
4	1	1
	1.0	2.0
6	3	2

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13. ABSTRACT An NMR and EPR study of the reaction products of formaldehyde and N-methyl-hydrazine was conducted primarily to identify the radical species noted when 1,4-dimethyl-dihydro-s-tetrazine was prepared by the oxidation of 1,4-dimethyl-hexahydro-s-tetrazine with mercuric oxide. The radical was deep violet in ether solution, and generated an extremely complex ESR signal. NMR analysis demonstrated that the radical precursor was a reaction side product, and was only present when certain NMR peaks were present. The NMR data coupled with the assignment of the spectrum generated indicated that the precursor was 1,5-dimethyl-hexahydro-s-tetrazine, and the radical was 1,5-dimethyl-verdazyl. This thesis reports the first aliphatic verdazyl. Complete NMR, ESR, and molecular orbital data are documented as is a unique computer method for assigning ESR spectra. In addition, mass spectrographic, UV/visible, IR, and chromatographic methods/data are discussed.		

14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
1,5-dimethyl-verdazyl							
1,5-dimethyl-hexahydro-s-tetrazine							
1,4-dimethyl-hexahydro-s-tetrazine							
ESR							
NMR							
Formaldehyde							
N-methyl-hydrazine							

Thesis

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